

# Optimization of crayon production from rumex abyssinicus dye extract

By: Naol Bekele



A Thesis Submitted to  
The department of Chemical Engineering  
School of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's in  
Chemical Engineering (Process Engineering)

Office of Graduate Studies  
Adama Science and Technology University

Adama  
March, 2021

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## APPROVAL OF BOARD OF EXAMINERS

We, the undersigned, members of the board examiners of the final open defense by Naol Bekele Deriba, have read and evaluated his thesis entitled “**Optimization of crayon production from rumex abyssinicus dye extract**” and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirement of the degree of masters in chemical engineering.

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## DECLARATION

I hereby declare that this MSc entitled “**Optimization of crayon production from rumex abyssinicus dye extract**” in partial fulfillment of the requirement for the award of the degree of masters of science in process engineering is my original work carried out under the supervision of Dr mulugeta and Dr Tatek, Department of Chemical and Process Engineering, Adama Science and Technology University, Ethiopia. It has not been presented for degree in any other university, and all source of materials used for this thesis have been duly acknowledge.

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## LIST OF ACRONYMS

ANOVA	Analysis of Variance
AOAC	Associates of Analytical Chemistry
$CO_2$	Carbo dioxide
E	Elongation
FTIR	Fourier transforms infrared spectroscopy
G	Gram
h	Hour
ml	Milliliter
mm	Millimeter
$R^2$	Regression Coefficient
RSM	Response Surface Methodology
S	Stress
TGA	Thermogravimetric Analysis
UV-VIS	Ultra-violate visible spectrophotometry

## **ABSTRACT**

*In this study, the natural dye was extracted from 'rumex abyysinicus' by using soxhlet extraction and applied for crayon formulation, because of its good affinity, brilliant colors, non-allergic on the human being, locally accessibility, nontoxicity, and not damaging to the environment. The objective of this thesis was to investigate proximate and mineral analysis, effects of extraction time, solid-liquid ratio, and particle size impact on the yield of dye, and characterization of the dye obtained by UV-vis spectroscopy and FT-IR to determine functional groups. Design of experiment for RSM three-variable and three-level was used to analyze and optimize the effect of extraction time (1.5h, 3.25h, and 5h), dried ground rumex abyssinicus to the volume of ethanol ratio of (0.05g/ml, 0.075g/ml and 0.1g/ml) and particle size (0.355mm-0.71mm) to obtain the maximum yield of dye. Maximum yield of dye (0.53%) was obtained at extraction time of 5hr, particle size (0.355mm-0.5325mm) and rumex to volume ethanol ratio (0.075g/ml). FT-IR was determined functional group present on the dye and nature of bands and UV-vis spectra were showed absorbance of dye (0.908) at  $\lambda_{max} = 281n$ . And also, this study investigated the effect of paraffin wax, talc, extracted dye, and temperature on the formulated crayon. And the crayon was characterized by using UV-vis spectroscopy, FT-IR, TGA, tensile strength, visibility, and durability by comparing it with commercial crayon. Design of experiment for RSM of four-variable and three-level was used to analyze and optimize the effect of paraffin wax (4g to 8g), dye (0.5g to 2g), talc (5g to 9g), and temperature (80°C to 100°C) and also at a constant value of stearic acid 0.5g and bee wax 1g to determine maximum absorbance of crayon color by using UV-vis spectra. UV-vis showed a maximum absorbance of (0.830) at  $\lambda_{max} = 298.7nm$  for the crayon formulated and the commercial crayon was (0.68) at  $\lambda_{max} = 305.5nm$ , Tensile Strength of formulated crayon was 1.48N/mm<sup>2</sup> and commercial crayon was 1.53N/mm<sup>2</sup> respectively and the percentage of elongation of E (%) break strength of formulated crayon was 1.34% and for the commercial was 1.4%.*

# CHAPTER ONE

## 1. INTRODUCTION

### 1.1 Background

Modern crayons are a combination of pigment or dye and wax. The origin of the word crayon is believed to go back to 1644, a diminutive of the French word craie (chalk) and the Latin word crate (Earth). The use of pigment mixed with wax has been traced back to the Egyptians who used a technique of combining hot beeswax with colored pigment to bind color into stone in a process known as encaustic painting. The image was fixed in place by heating. A similar method was used by the Romans, the Greeks, and indigenous people in the Philippines around 1600-1800 [1]. The crayon drawing in fine arts has a very wide range of applications, from rough sketches to detailed illustrations.

Dyes are organic compounds widely used for imparting color [2]. Two types of dyes 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 a repulsive smell, and are poisonous to human beings. Natural dyes, on the other hand, are easily accessible and have a less damaging effect on human health because of the way, they are extracted. Although they are not as pure and fast as synthetic dyes, most of them possess qualities such as good affinity, brilliant colors, and fastness properties which make them compete favorably with synthetic dyes [3].

The use of natural dyes that are nontoxic and non-allergic on materials has gained significant importance due to ever-increasing awareness and concerns regarding environmental pollution as in the case of synthetic dyes [4].

Because of these issues, persisting with natural alternative materials for dyeing, this study attempted the use of plant constituents from *rumex abyssinicus* (mekmeko) for the color of crayon. *Rumex abyssinicus* is widespread in tropical Africa, most commonly in higher lands, particularly in central and eastern Africa and Madagascar. The plant is generally considered as a native of Africa, especially Ethiopia (*Abyssinicus* means from Abyssinia, Ethiopia). It is locally endemic to Ethiopia, and

the plant is referred to as mekmeko in the Amharic language [5]. Traditionally, mekmeko root part has been extensively used in Ethiopia for dyeing of the palms of ladies' hands and feet. It yields black, yellow, and red colors.

*Rumex Abyssinicus*, which belongs to the family Polygonaceae is a perennial herb, up to 3m tall, the leaf of the plant is usually sagittate, and inflorescence, and much-branched. The rhizomes are used to refine butter and give it a rich black color. Natural coloring matters depending upon their nature can also be extracted by organic solvent extraction (ethanol) [6] by considering the design of the experiment to analyze and optimize the effect of extraction time, solid-liquid ratio, and sieve assize analysis. The recently established use of *Rumex abyssinicus* material is the extraction of dye for the application of color.

Waxes are a diverse class of organic compounds that are hydrophobic, malleable solids near ambient temperatures. They include higher alkanes and lipids, typically with melting points above about 40 °C (104 °F), melting to give low viscosity liquids. Waxes are insoluble in water but soluble in organic, non-polar solvents. Natural waxes of different types are produced by plants and animals and also occur in petroleum. Among the waxes synthesized by many plants and animals, those of animal origin typically consist of wax esters derived from a variety of carboxylic acids and alcohols. Beeswax shows low water vapor permeability, low minimum film-forming temperature, and forms continuous films. The water vapor permeability of rice wax is higher compared to beeswax, but there is no minimum film-forming temperature in the temperature range of 20 °C – 80 °C and the appearance of the rice wax films is homogeneous. These waxes are composed of different chemical compounds in various ratios depending on their origin and environmental factors, such as long-chain esters, hydrocarbons, long-chain alcohols, long-chain carboxylic acids, and sterols [7].

Paraffin wax is solid at room temperature, insoluble in water, burns readily, and melts at a temperature (47°C-70°C). Paraffin wax is used in the manufacture of lubricants, crayons, surgery, stoppers for acid bottles, electrical insulation, floor polishes, and cosmetics [8]. Moreover, it is a white or colorless soft solid hydrocarbon molecule containing between twenty and forty carbon atoms derived from petroleum, coal, or oil shale. Paraffin waxes are saturated hydrocarbon

mixtures that usually consist of a mixture of different alkanes. They are characterized by straight or branched carbon chains with the generic formula  $C_n H_{2n+2}$ .

Talc belongs to the general mineral family of the layered silicates which are present in nature and are composed of crystalline hydrous magnesium silicate. In combination with magnesite, it is available worldwide. It is also possible to find pure talc. Commercial use is possible after sorting where talc crystals are milled or micronized to fine powders. Talc structure is soft and chemically inactive with bright white color in general. Its color may be changed by staining with iron or impurity by other minerals. It is not specifically deemed dangerous and is classified as irritant dust in powder form. Two types of talc: industrial and cosmetic, are used in paper plastic, rubber, paint, and cosmetic manufacturing work. Talcum powder is widely used in medical and pharmaceutical products and is usually applied to the skin to reduce friction and prevent rashes [9].

The present work relates to crayons, and in particular, to crayons for coloring. The first box of crayons has, for generations of children, marked an initiation into the life of school and learning. For many children, it is the first experience of contacting paper with a writing instrument. Crayons have historically contained a predominant concentration of paraffin, a wax such as Bee's wax or Carnauba wax, stearic acid, and a non-toxic pigment to impart color [10]. The process by which the paraffin-based crayons are made includes mixing stearic acid and pigments with paraffin heated to 160°F. Once mixed, and further heated to 20°F -250°F., the molten solution is added to molds. When cooled, the crayons are removed from molds and packaged [11].

## **1.2 Statement of the problem**

Mekmeko (*Rumex Abyssinicus*) is an available plant, and it has been used by mothers for long time. Mostly this plant is left tested in forests and is also rarely used as animal feed. However, there is the intention to make use of it by extracting dye from the plant species from its root. Natural dyes are eco-friendly, renewable, and biodegradable and the dye extracted is known to be skin-friendly and may also provide health benefits to the wearer.

The natural products sector of Ethiopia is dependent on international trade for its commercial success as indicated in the literature part crayon demand in a different section in our country. One of the major problems of the crayon production industry in the country is unavailability of

small scale adapted technology based on the socio-economic level of the rural community, lack of information on the social and economic benefits to be derived from the industrial utilization of aromatic plants. And the low priority given by the government has been a major factor impeding the development of the industry in Ethiopia like other small-scale crayon pencils production industries is a scarcity of adapted technological input in the required level and crayon produced from a synthetic dye those impacts on the environment and human health.

The availability of raw material in our country as Ethiopia is importing crayon pencils value-added products from the international market at a high price. There is an opportunity to substitute the imports. The increasing importance of crayon pencils as handwriting aid besides their traditional role has opened up wide opportunities for global marketing. Although natural dye production from rumex is not started in Ethiopia following the growth of chemical industries its demand has increased from time to time, and also the limited availability of crayons to children in suburban and rural areas and the accessibility issues.

The advantage of organic dye from rumex root has to replace the synthetic dye due to the lower environmental impact and simple processing methods. Hence, rumex root 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 organizations, and reduces the utilization of synthetic dyes.

## **1.3 Objectives**

### **1.3.1 General objective**

Formulation, optimization, and characterization of crayon by using extract dye from rumex abyssinicus

### **1.3.2 Specific objectives**

The specific objectives of this study are;

- ❖ To extract organic dye from root of rumex abyssinicus (mekmeko)
- ❖ To optimize dye by studying the effect of process parameters (i.e., time, solid-liquid ratio, and particle size )
- ❖ To characterize the optimal dye by considering the maximum yield obtained

- ❖ To formulate ,optimize ,and characterize the crayon by considering absorbance of color and study the effect of process parameters (paraffin wax, talc, dye, and temperature)

## **1.4 Significance of the study**

This research has benefits for many Ethiopian children who need to use crayon pencils in their life.

Hence, this study should be significant in the sense that it will:

- ✓ Provide a means to exploit and manage local resources.
- ✓ To increase the amount of crayon that is needed by students
- ✓ To reduce importing crayon pencil value-added products from the international market at a high price.
- ✓ Minimize the impact of synthetic dye since a high concentration of natural dyes has the potential to replace it
- ✓ Enhance knowledge and understanding on the potential utilization of rumex abyssinicus root to bring economic benefit
- ✓ Provide as alternative raw material for crayon formulation

## **1.5 The scope of the study**

The main objective of this research is directed towards the extraction of rumex root for dye synthesis and the application of the extracted dye for crayon production. It includes a collection of the root of rumex abyssinicus, washing of the root, dry by using oven drier and extraction of dye using soxhlet extraction method, investigation of the main and interaction effect of extraction factors (sieve size, solid to liquid ratio, and extraction time), determining the optimum conditions for dye extraction and characterization of the root of rumex optimized by using oven drier and muffle furnace for proximate analysis (moisture content and ash content ), UV- Vis spectra pattern and FTIR spectroscopy used for characterization of the optimal yield of dye and The crayon formulated by mixing extracted dye with paraffin wax, talc, bee wax, and stearic acid. Through this study, the product of crayon should be determined by optimizing the main effect of parameters temperature, paraffin wax, talc, and dye mixing ratio were studied and

The characteristics of the optimally formulated crayon were evaluated by exploring the structural changes via a series of tests like TGA, UV- Vis spectra pattern, tensile strength, FTR, and for enhancing the product of crayon.

## CHAPTER TWO

### 2. LITERATURE REVIEW

#### 2.1 General

There are over 100,000 available dyes and about  $7 \times 10^5$  tons of dyestuff manufactured yearly [12]. 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. Since 1856, 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 society. However, synthetic dyes are mostly toxic and carcinogenic. Moreover, this dye has become one of the key sources of groundwater 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 to be released together with the effluents [13].

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 a plant such as seeds, flowers, leaves, barks, and roots can be used to extract dyes [14].

#### 2.2 *Rumex Abyssinicus* (Mekmeko)

*Rumex abyssinicus* Jacq (Family: Polygonaceae) is known by the Amargna (*also in Guragigna*) and *Ge'ez* names meqmeqo and *etse birhan*, respectively. Its other vernacular names include

mokmoko, mekimeko (Tigrigna, Amargna), choldia, dangago (Wollaitigna), chole eye (Dawar'gna), magmagno (Saho) and sholsholo (Me'en'gna). In East Africa, it is known by the names gentamana, kinyonywe, and omuka. Its English common name is spinach [15]. *Rumex Abyssinicus*, which belongs to the family polygonaceae is a perennial herb, up to 3m tall, the leaf of the plant is usually sagittate, and inflorescence, and much branched. The rhizomes are used to refine butter and give it a rich yellow color. The family polygonaceae comprises some 5 genera and 200 species largely concentrated in temperate areas of the northern hemisphere and tropical subtropical mountains. Some of the species which are found in Ethiopia are *Rumex epalensis*, *Rumex crispus*, *Rumex vesicarius*, *Rumex Abyssinicus*, *Rumex nervosus*, *R. obtusifolius* [6].



Figure 2.1: *Rumex Abyssinicus*

### 2.2.1 Range

Tropical Africa - mainly in the drier areas from Nigeria to Ethiopia, south to Angola, Zambia and Mozambique. *Rumex abyssinicus* is widely spread in the highlands of tropical Africa. It is widespread throughout Ethiopia at altitudes between 1200 and 3300m. It is a common and tolerated weed in fields and plantations. It also occurs along paths and water, in secondary scrub, grassland, and margins of the rain forest. This plant species will remain locally an important vegetable from the wild [16].

### 2.2.2 Cultivation Details

Plant of mainly higher elevations from 750 - 3,300 meters, in the tropics. In Tanzania, the plant thrives on volcanic soils and sandy loams, where the mean annual rainfall is 1,100 - 2,200mm.

Succeeds in most soils but prefers a deep fertile moderately heavy soil that is humus-rich, moisture-retentive but well-drained, and a position in full sun or part shade. Removing the flowering stem, before it can flower, increases the yield of leaves [17].

### **2.2.3 Known Hazards**

Plants can contain quite high levels of oxalic acid, which is what gives the leaves of many members of this genus an acid-lemon flavor. Perfectly alright in small quantities, the leaves should not be eaten in large amounts since the oxalic acid can lock-up other nutrients in the food, especially calcium, thus causing mineral deficiencies. The oxalic acid content will be reduced if the plant is cooked. People with a tendency to rheumatism, arthritis, gout, kidney stones, or hyperacidity should take especial caution if including this plant in their diet since it can aggravate their condition [17].

### **2.2.4 Edible Uses**

Tender young shoot and leaves-raw or cooked. An acid flavor, they are widely used as a vegetable, either cooked alone or together with other vegetables. They are also eaten raw as a snack. The stem is chewed like sugar cane for its sweetness. A dye obtained from the rhizome is used in butter as a condiment, to give it a rich yellow color and also as a protection against rancidity (Ruffo, C.K.: Birnie, A. & Tengnas, B., 2002). Traditionally, the root part of mekmeko is used in butter as a condiment for protection against rancidness. Mekmeko has been investigated by various researchers for treating skin problems and other medicinal applications [18].

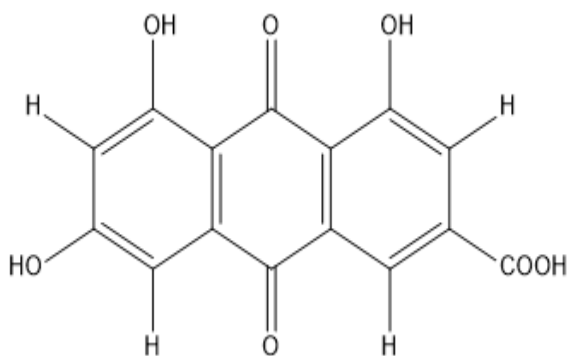
Traditionally, a mekmeko root part has been extensively used in Ethiopia as for the palms of the hand feet red by ladies. Recently established the use of mekmeko material for the preservation of goat skins [5]. A yellow and a red dye can be obtained from the rhizome. It is used for coloring wickerwork and mats of grass and raffia, and also to impart a red color to the feet and hands of women. The crushing plants are used to scour clean cooking pots that have been blackened over the fire, and also to remove grease. Leaves of various Rumex species are very good at removing dirty oil from the skin - simply crush the leaves to release the sap and rub them over the dirty area [19].

### 2.2.5 Medicinal Uses

The plant is astringent, depurative, and hemostatic. It is used to treat jaundice and related liver diseases; scrofula; stomach-ache; neck ache; and low blood pressure. The sap of the aerial parts is applied as a treatment for pneumonia and cough. Applied externally, the plant is used fresh or dried to treat wounds, sores, and parts affected by scabies. A leaf-compress is applied to areas of rheumatism [20]. In Ethiopian traditional medicine, the rhizomes are used for treating malaria, gonorrhea, poisoning, hepatitis, constipation, sciatic neuralgia, hypertension, migraine, rheumatism, breast cancer, stomach distention, earache, liver disease, hemorrhoid, typhus, rabies, scabies, and wound. In *Ada'a* district, the bruised eye is treated by drinking a solution prepared by boiling the roots with butter. The leaf is used for gonorrhea and abscesses. In Ethiopian traditional veterinary practice, *Mekmeko* is also used to treat animals with blackleg and scabies.

### 2.2.6 Chemical Composition

The chemical composition constitute an important class of compounds with important biological properties. These compounds elaborated both by higher and lower plants are also one of the most well-known naturally occurring pigments. They range in color from black to orange and also to red. Anthraquinones and related compounds in higher plants are located in all parts of the plant, including root, bark leaves, seeds, and flowers often occur as glycosides. Figure (2.2) shows the chemical composition of the compound that occurred in *rumex abyssinicus*.



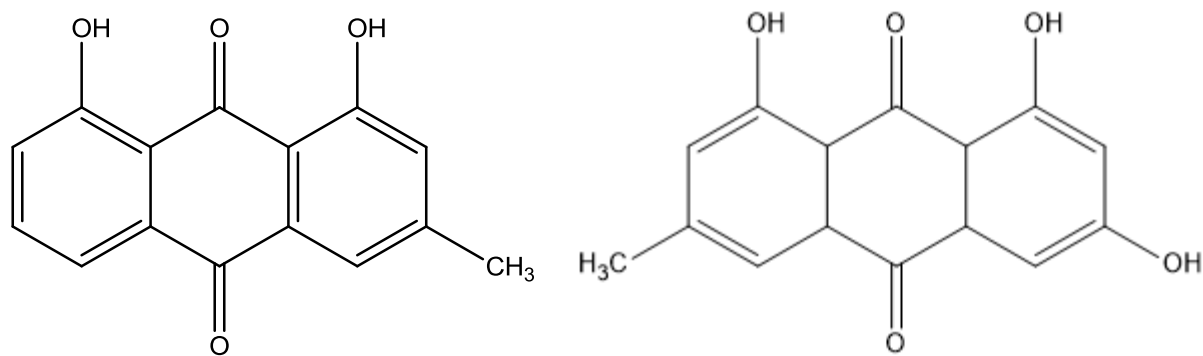


Figure 2.2: component occurred in dye extracted from *Rumex Abyssinicus* [5]

## 2.3 Dye

A dye is a colored substance that has an affinity to the substrate to which it is being applied. Dyeing was known as early as in the Indus Valley period (2600–1900 BC); this knowledge has been substantiated by findings of colored garments of cloth and traces of madder dye in the ruins of the Indus Valley Civilization at Mohenjodaro and Harappa. Man has always been interested in colors; the art of dyeing has a long past and many of the dyes go back into prehistory. It was practiced during the Bronze Age in Europe. The earliest written record of the use of natural dyes was found in China dated 2600B.C.[21].

The newfound awareness of human safety and environmental conservation has kindled fresh enthusiasm for natural sources of colors. Natural colorants or dyes derived from flora and fauna are believed to be safe because of non-toxic, non-carcinogenic, and biodegradable [22]. Traditional sources of colorants include natural products such as flavonoids and anthraquinones produced by plants and animals. For example, carminic acid, a deep red anthraquinone produced by scale insects is now used as a pigment in paints, crimson ink, cosmetics, and food colors [23].

### 2.3.1 Natural Dye

The majority of natural dyes are from plant sources: roots, berries, bark, leaves, and wood, fungi, and lichens. The word "natural dye" covers all the dyes derived from natural sources like plants, animals, and minerals. Natural dyes are mostly non-substantive and must be applied on textiles with the help of mordant, usually a metallic salt, having an affinity for both the coloring matter and the fiber. Transition metal ions usually have strong coordinating power and/or capable of forming weak to medium attraction/interaction forces and thus can act as bridging material to

create substantively of natural dyes/colorants when a textile material being impregnated with such metallic salt (i.e. mordant) is subjected to dyeing with different natural dyes, usually having some mordant able groups facilitating fixation of such dye/colorant. These metallic mordant after combining with dye in the fiber forms an insoluble precipitate or lake and thus both the dye and mordant get fixed to become wash fast to a reasonable level [24]. Some of the pros and cons of natural dyes are given in Table (2.1).

Table 2.1: Advantages and disadvantages of natural dye [4]

Advantage	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 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 a few have good fastness to light and washing
Have pharmacological effects and possible health benefits	Some of the mordants are harmful
Technology for production could vary from simple aqueous to complicated solvent system and super crucial fluid extraction techniques	Mostly used for protein and cellulosic fibers

### 2.3.2 Synthetic Dye

Synthetic dyes are man-made. These dyes are made from synthetic resources such as petroleum by-products and earth minerals. The first human-made organic aniline dye, mauveine, was discovered serendipitously by William Henry Perkin in 1856, the result of a failed attempt at the total synthesis of quinine. Other aniline dyes followed, such as fuchsine, safranine, and induline. Many thousands of synthetic dyes have since been prepared [25].

Basis for color

Unlike most organic compounds, dyes possess color because they

1. Absorb light in the visible spectrum (400–700 nm),
2. Have at least one chromophore (color-bearing group),
3. Have a conjugated system, i.e. a structure with alternating double and single bonds, and
4. Exhibit resonance of electrons, which is a stabilizing force in organic compounds [26]

When any one of these features is lacking from the molecular structure the color is lost. In addition to chromophores, most dyes also contain groups known as *auxochromes* (color helpers), examples of which are carboxylic acid, sulfonic acid, amino, and hydroxyl groups. While these are not responsible for color, their presence can shift the color of a colorant and they are most often used to influence dye solubility [26].

## 2.4 Extraction of Natural dyes

### 2.4.1 Extraction Methods

As natural dye-bearing materials contain only a small percentage of coloring matter or dye along with the number of other plant and animal constituents such as water-insoluble fibers, carbohydrates, protein, chlorophyll, and tannins, among others. Extraction is an essential step not only for preparing purified natural dyes but is also required to be carried out by users of crude dye-bearing materials. 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. Nature and solubility characteristics of the coloring materials need to be ascertained before employing an extraction process [27].

#### 2.4.1.1 Aqueous extraction

Aqueous extraction was traditionally used to extract dyes from plants and other materials. In this method, the dye-containing material 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 (Preferably copper or stainless steel) 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 plant remnants. The process of boiling and filtering is repeated to remove as much dye as possible. Generally, centrifuges are used to separate residual matter. The use of trickling filters can ensure the removal of fine plant material particles and ensure better solubility of the purified natural dye. 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 [28].

Similarly, for extraction purposes from mekmeko, root samples need careful washing with water, before air drying under the shade and at room temperature. Conventional solid-liquid aqueous extraction (1,10 w/v) from mekmeko powder can be done by a round- bottom flask (without stirring) in a stirred water bath heated at 80 °C for 2 hr. The obtained aqueous extract shall be filtered by using a cotton cloth and concentrated to 20–25% solids [18].

#### **2.4.1.2 Solvent Extraction**

Natural coloring matters depending upon their nature can also be extracted by organic solvent. The 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. The water/alcohol extraction method can 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 a larger number of chemicals and coloring materials can be extracted. Acid or alkali can also be added to alcoholic solvents to facilitate hydrolysis of glycosides and the release of coloring matter. Purification of extracted color is easier as solvents can be easily removed by distillation and reused. Extraction is performed at a lower temperature thus chances of degradation are fewer. The extraction yield is thus higher as compared to the aqueous method as a larger number of chemicals and coloring materials can be extracted [29]. The disadvantages of the method are the presence of toxic residual solvents and their greenhouse effect [30].

#### **2.4.1.3 Enzymatic Extraction**

This method of extraction uses the enzymes produced by the microorganisms present in the natural resources for assisting the extraction process. As plant tissues contain cellulose, starches,

and pectin's as binding materials, commercially available enzymes including cellulose, amylase, and pectinase have been used by some researchers to loosen the surrounding material leading to the extraction of dye molecules under milder conditions [4]. It is collected, washed, and after removing excess water is pressed into cakes. The enzymatic method is similar to aqueous extraction with the exception that this method does not require high temperatures. The microorganisms disintegrate the coloring matter binding substances naturally. Long extraction time, need for immediate extraction of pigments after harvesting, foul smell due to microbial action, and so on, are some of the disadvantages of this method.

#### **2.4.1.4 Supercritical Fluid extraction**

This extraction method 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. A supercritical fluid can dissolve many substances like a liquid, as the solubility of a substance in any solvent is higher at higher pressure and temperature and such conditions are needed to maintain the gas in the supercritical state. Supercritical fluid extraction using  $CO_2$  is a good alternative to solvent extraction as it is non-toxic, cheap, easily available, and does not leave residues [30]. Supercritical fluid extraction is the usage of the fluid at its supercritical stage. Accepted as gas  $CO_2$  was the generally used fluid in this method. Although it requires a special equipment, it is a fast process and requires less amount of sample, and solvent than conventional solvent extraction [31].

## **2.5 Characterization of natural dyes**

### **2.5.1 Fourier Transform Infrared spectroscopy**

Fourier Transform Infrared (FTIR) spectroscopy is a principally useful analytical method because of its versatility. Its distinct advantage over other forms of spectral data acquisition is that it can look at all the wavelengths of a spectral region simultaneously, rather than one wavelength at a time. Such an approach saves time dramatically and utilizes light more efficiently [32]. 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 homopolymer, copolymer, and polymeric materials, in general, can be obtained using Infrared (IR) spectroscopy FTIR spectrum of the produced natural

dye after purification is demonstrated. The IR spectroscopy of dye extract shows the range of Phenol compound is at the peak of  $3400.5\text{cm}^{-1}$  ( $3200\text{-}3550\text{cm}^{-1}$ ) and this strong signal corresponding to the characteristic O-H vibration, Alkanes are obtained at  $2922.16\text{cm}^{-1}$  ( $2850\text{-}2950\text{cm}^{-1}$ ),  $1723.431\text{cm}^{-1}$  is carboxylic acid of C=O stretch,  $2086.48\text{cm}^{-1}$  the peak is alkyne,  $1454.33\text{cm}^{-1}$  peak is H-C-H stretch and C=C aromatic group vibrational frequency, amines are at  $1168\text{cm}^{-1}$  and  $721.38\text{cm}^{-1}$  peak is in C-H bending [4].

### **2.5.2 UV-Vis spectral**

For characterization, purified aqueous dye solution separately and is subjected to wavelength scan 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 wavelengths shows its main hue, absorption, etc. Peaks and troughs in the visible zone thus indicate the main color and absorption. UV-Zone with/without peaks shows the property of the dye under UV-light, this may be correlated with fastness behavior [15].

### **2.5.3 Thermographic analysis (TGA)**

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature with constant heating rate, or as a function of time with constant temperature and/or constant mass loss [33]. TGA displays the mass of the sample versus temperature.

## **2.6 Factors affecting the extraction of dyes**

Many factors affect the process of dye production, including temperature, extraction time, and mass to volume ratio. And extraction of bioactive compounds is influenced by various process parameters such as solvent composition, 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 [4].

### **2.6.1 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 a solvent. Therefore, more water usage in extraction

may lead to higher energy consumption. The material to liquor ratio affects the dye molecules to be congested, and they collide with each other to increase the affinity of dye molecules for each other [34]. The soxhlet extraction process is also affected by the solid to liquid ratio.

### **2.6.2 Effect of extraction time**

Extraction time is one of the important factors for the 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 extraction time 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, a suitable duration can be selected for the process [35]. Extraction time is one of the important factors for the extraction of pigments and colors from plant materials. The extraction yield is normally increased rapidly at the initial stages of extraction but ends with a slower extraction rate. The optimum time of the extraction for maximum natural dye extraction varies with the extraction condition [4].

## **2.7 Overview of wax**

Waxes are usually relatively stable nontoxic substances, which mankind has used for a variety of purposes since prehistoric times. The English word wax is derived from the Anglo-Saxon wax, which was the name indicated to the natural material gleaned from the honeycomb of the bee [36]. In modern times the word has occupied a broader significance and is commonly applied to all wax-like solids and liquids bring into being in nature. Synthetic compounds which are not wax from the standpoint of chemical composition, but do have waxy physical characteristics, are contained within because of their value in technical use as wax substitutes.

Originally the word wax would have signified beeswax almost exclusively, however, the following can be given as a description: Historically, waxes are substances having characteristics to a certain extent like beeswax; Chemically, waxes are esters of fatty acids and monohydric fatty alcohols; Physically, waxes are water-repellant solids having advantageous degrees of plastic characteristics; functionally, waxes now consist of several substances that can be used in place of natural waxes as ingredients in preparations. The major modules of waxes are planted, animal (including insect), mineral (including petroleum), and synthetics [37].

Current vegetable waxes have been used in industry since the mid-nineteenth century, for example in health precaution products. Partially synthetic hard waxes based on montan wax are quite analogous to naturally happening vegetable ester waxes in their structure and application characteristics. They are analogous in their environmental characteristics and are also nontoxic [36].

Crude montan wax itself also belongs to the naturally occurring waxes of vegetable origin such as carnauba wax and candelilla wax. Montan wax is a fossilized vegetable wax extracted from lignite's, principally from the central German brown coal reserves west of the Elbe River. Montan waxes of minor quality and quantity have also been mined in Australia, New Zealand, Czechoslovakia, Russia, Great Britain, China, and the United States. Prehistoric palm trees as well as laurel, camphor, and cinnamon trees are indicative of subtropical flora [36]. Throughout the earth's history, specific geological conditions have resulted in the formation of brown coal reserves in which the non-decomposed waxes of the earth's early vegetation have accumulated over millions of years.

## **2.8 Types of wax**

Waxes are commonly well-defined utilizing hydrophobic organic substances having medium and long-chains of carbon atoms. Based on waxes, they are categorized as synthetic or natural waxes. Natural waxes activate from animals, plants, or fossil fuels like petroleum or coal. These waxes are composed of diverse chemical compounds in several ratios based on their origin and environmental factors, e.g. long-chain esters, hydrocarbons, long-chain alcohols, long-chain carboxylic acids, sterols, etc [7]. Certain of these compounds only exist in minor amounts [38]. Furthermore, their physical properties are obtained by the molecular structure rather than by molecular size [7]. Besides, they are categorized as renewable, non-toxic, cost-competitive, and their potential to substitute petrochemical waxes [39].

### **2.8.1 Natural Wax**

Waxes are a various category of hydrophobic organic compounds, malleable solids, close ambient temperatures. They include higher alkanes and lipids, typically with melting points above about 40 °C (104 °F), melting to provide low viscosity liquids. Waxes are insoluble in water but soluble in organic, non-polar solvents. Natural waxes of various categories are

produced by plants and animals and also happen in petroleum. Waxes synthesized by various plants and animals, those of animal origin classically contain wax esters derived from a diversity of carboxylic acids and alcohols. In waxes of plant origin, characteristic combinations of esterified hydrocarbons may predominate over esters [39]. Beeswax is a naturally happening animal wax, which is formed using honeybees and can be characterized as inert with high plasticity. It shows viscoelastic behavior due to the existence of fatty acids [40] and has a low melting point. Beeswax is the most commercially used natural wax [41] and its application in food products is boundless. Candelilla wax is a plant wax gained from the leaves of *E. antisiphilitica Zuccarini*. It contains the highest amount of hydrocarbons compared to other waxes and therefore, it is listed as the wax with very low water vapor permeability [42].

### 2.8.1.1 Bee Wax

Depend on the wax used for basics, which is probably the main use, not only this it also use for the following application: cosmetics 25-30%, pharmacy 25-30%, candles: 20% and other purposes: 10-20%. According to the above-mentioned type of wax it is well to use bee wax for the formulation of shoe polish since bee wax is waxy organic raw materials, non-toxic, the flexibility of operation, easy availability in Ethiopia compared to other types of wax, due to this it is recommended using bee wax as a raw material for shoe polish formulation [39]. From insect waxes beeswaxes have comparatively low melting points; in pharmacopeias the melting point is 61 – 66 °c and usually quoted as 63 °c to 65 °c. And the structure of bee wax is in figure below.

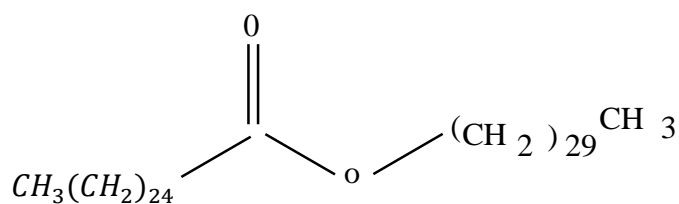


Figure 2.3: beeswax structure

Beeswax is secreted by worker honeybees from four pairs of wax glands on the underside of the abdomen. Bees require wax as a building material for their combs. They form it in their wax glands which are fully established in 12 to 18 day-old workers. In older bees the wax glands diminish their action, but, in emergency conditions, wax extract can be activated. The main raw materials for wax creation are carbohydrates i.e. the honey sugars fructose, glucose, and sucrose.

The ratio of sugar to wax can differ from three to 30:1. The stronger the colony, the smaller the ratio, and the more economical the wax production for the colony [43]. Current vegetable waxes have been used in industry since the mid-nineteenth century, for example in health attention yields. Partially synthetic hard waxes depend on montan wax are quite like to naturally happen vegetable ester waxes by considering their structure and application characteristics. They are similar according to their environmental characteristics and are also non-toxic [44].

### **Quality Specification and storage condition for the beeswax**

Beeswax should only be stored in its rendered, clean form. Before rendering, it will quickly be attacked by wax moths, which can destroy large quantities of wax in short periods. Clean wax in large blocks is not attacked by wax moths. Storage should be in cool dry places and never in the same room with any kind of pesticide. Wax will slowly crystallize over time and as a consequence become harder, but this process is reversible without any damage, just as with crystallized honey. Wax can be stored for very long periods without losing its major characteristics as items from Egyptian graves more than 2000 years old have shown

Beeswax, when sold in solid blocks should always both be clean and have color and odour characteristics. Though adulteration is easy (usually with cheap waxes), its detection is only possible with chemical tests. Quality standards for wax are set in most countries according to their pharmacopeias (a book describing drugs, chemicals, and medical preparation: especially one issued by an officially recognized authority and serving as a standard). A few industries like the Japanese cosmetic industry but also the American Wax Importers and Refiners Association specify their limits. Standards may vary considerably from country to country and manufacturer to manufacturer [43].

#### **2.8.1.2 Paraffin wax**

It is solid at room temperature, insoluble in water, burns readily, and melts at a temperature (47°C-70°C). Paraffin wax is used in the manufacture of lubricants, crayons, surgery, stoppers for acid bottles, electrical insulation, floor polishes, and cosmetics. Common applications for paraffin wax include lubrication, electrical insulation, and candles and fruit waxing [45]. Paraffin wax is a tasteless and odorless white translucent solid. The source of paraffin wax is petroleum. It is produced following petroleum refining by dewaxing light lubricating oil stocks. It consists of a mixture of solid aliphatic hydrocarbons of high molecular weight such as  $C_{36}H_{74}$ . Its

molecular formula is  $C_n H_{2n+2}$  [46]. Paraffin wax can be defined as a fraction of petroleum dominated by n-alkanes that are solid at ambient temperature [47]. It contains above  $C_{8+}$ , smaller amounts of isoalkanes, cycloalkanes and aromatics. Paraffin waxes are chemically stable and have a negligible degree of subcooling during nucleation. There is no phase separation, and the phase change process only results in a small volume change [48]. Paraffin waxes are commonly classified in the petroleum industry literature as paraffin, intermediate and microcrystalline type [49].

### **2.8.1.3 Properties and classification of paraffin wax**

The paraffin wax properties including the values of wax density, melting point, flash point, and autoignition temperature. The density varies between 0.88 and 0.94 g/cm<sup>3</sup> [50]. The melting point ranges from 47 to 65°C [8]. The flashpoint equals 390°F or 198°C. The autoignition temperature is reached at 473°F or 245°C [8]. The paraffin wax has a molar mass equal to 785 g/mol and a C/O ratio of 18.8/1 [50]. Its common properties are water repellency, smooth texture, low toxicity, and freedom from objectionable odor and color [51]. Paraffin waxes contain carcinogens since they are processed using toxic material. The threshold limit value for paraffin wax is 2 mg/m<sup>3</sup>. Paraffin wax is soluble in benzene, ligroin, warm alcohol, chloroform, turpentine, carbon disulfide, and olive oil. It is insoluble in water and acids. Paraffin wax is combustible and has good dielectric properties. Paraffin wax grades are yellow crude scale, white scale, and refined wax. Paraffin waxes are also graded by melting point and color. The higher-melting grades are more expensive.

Paraffin waxes are classified according to oil content, melting point, and the amount of processing put in. At the simplest level, Slack Wax, a by-product of base oil refining, is the feedstock from which different grades of more sophisticated waxes are produced. Fully-refined waxes are white, odorless and tasteless, and typically have less than 1% oil content. They are widely used for candle making and in the packaging industry as wax coatings for paper, film, and foil substrates including corrugated boards, cups, and containers. Waxes are marketed in either liquid or solid-state [52].

### **2.8.1.4 Characterization of Paraffin Wax:-**

Paraffin waxes are saturated hydrocarbon mixtures that usually consist of a mixture of different alkanes. They are characterized by straight or branched carbon chains with the generic formula

$C_n H_{2n+2}$ , the crystallization of the  $(CH_3)$  - chain release a large amount of latent heat. Both the melting point and latent heat of fusion increase with chain length, thus it has melting temperatures ranging from 23 to 67 °C [53]. They are white, semi-transparent, tasteless, and odorless solids with common properties such as smooth texture, water repellency, low toxicity, safe, reliability, predictable and non-corrosive. They are combustible and have good dielectric properties. They are soluble in benzene, ligroin, warm alcohol, chloroform, and carbon disulfide but insoluble in water and acids. They are commercially available, ecologically harmless, readily available, and inexpensive [53]. Their specific heat capacity is about 2.1 kJ/(kg\* K), and their enthalpy lies between 180 and 230 kJ/kg, quite high for organic materials. The combination of these two values results in an excellent energy storage density [54]. They have chemical stability, show little volume changes on melting, and have low vapor pressure in the melt form. Moreover, they have low thermal conductivity [55] and large volume change during a phase transition [56]. Because of these desirable characteristics of paraffin waxes. The application of phase change materials has found importance in various systems from energy storage to thermal protection [54].

### **2.8.1.5 Application of Paraffin Wax**

Paraffin wax is used in the manufacture of candles, paper coating, protective sealant for food products and beverages, glass-cleaning preparations, hot-melt carpet backing, biodegradable mulch (hot melt-coated paper), impregnating matches, lubricants, crayons, surgery, stoppers for acid bottles, electrical insulation, floor polishes, cosmetics, photography, an anti frothing agent in sugar refining, packing tobacco products, protecting rubber products from sun-cracking, and chewing-gum base. Waxy substances have been transformed and used by our ancestors as early as the neolithic period for a large range of activities [57]. They are used as waterproofing substances, illuminant, sealing agent but also for adhesive making and many other technical, medicinal, or symbolic purposes.

Additives are often mixed with these waxy materials to improve their properties. Resins are used to harden and color the material. Fatty materials increase the malleability and softness of waxes. Pigments and dyes color the material and starch are used as an extender. Common uses are for corrugated boxes, waxed papers, frozen food cartons and wrappers, paper cups, candles, cosmetics,

rubber antioxidants, lumber end seal, adhesives, protective coatings, food additives, cheese dipping, crayons, moisture barriers, polishes, modeling clay, plus many others.

## **2.9 crayon**

Crayons, in a form that can be held and colored with, are purported to have originated in Europe. Some of the first cylinder-shaped crayons were made with charcoal and oil. Pastels, composed of chalk and pigments are an art medium having roots with the modern crayon and stem back to Leonardo da Vinci in 1495. Conté crayons, used in Paris, a hybrid between a pastel and a conventional crayon were used since the late 1790s as a drawing crayon for artists. Various hues of powdered pigment eventually replaced the primary charcoal ingredient in the early 1800s product. Joseph Lemercier (1803 - 1884), considered by some of his contemporaries to be “the soul of lithography” was also one of the founders of the modern crayon. Through his Paris business circa 1828, he produced a variety of crayon and color-related products. But even as those in Europe were discovering that substituting wax for the oil strengthened the crayon, various efforts in the United States were also developing [1].

Wax crayons consist of natural and synthetic waxes, inorganic fillers (talcum), organic and inorganic pigments as well as emulsifying agents in the case of water-paintable crayons. They are manufactured in either a pressing process or a casting process (cast crayons). There are two types of wax crayons, water-resistant and water-paintable. Wax crayons are suitable for a wide variety of techniques such as Sgraffito, Encaustic or Ironing Technique, Wiping Technique, and Fabric Painting. In Sgraffito (scratching technique) several wax layers (from light to dark) are superimposed. The individual layers can then be made visible again or removed by scratching with a scraper or a sharp pencil. Encaustic is a technique where wax is melted and applied to the paper while it is still hot [19]. Crayons are supplied in tin cases, carry cases, and individual colors. For better handling and protection against color-staining, special crayon holders or paper wrappers, cardboard sleeves, plastic film-wrap or sliders can be used [19].

### **2.9.1 Talc**

The mineral talc has an ideal formula  $Mg_6Si_8O_{20}$  is hydrated magnesium silicate and Talc is a soft and commonly used mineral and considered inert, and produce no reaction, when used on skin and Talcum powder is widely used in medical and pharmaceutical products and is usually

applied to the skin to reduce friction and prevent rashes. Talcum powder can be contaminated with the associated phases like asbestos, dolomite, quartz, chlorite, and traces of metal oxide, which are considered to promote chronic diseases [58]. Talc belongs to the general mineral family of the layered silicates which are present in nature and are composed of crystalline hydrous magnesium silicate. In combination with magnesite, it is available worldwide. It is also possible to find pure talc. Commercial use is possible after sorting where talc crystals are milled or micronized to fine powders. Talc structure is soft and chemically inactive with bright white color in general. Its color may be changed by staining with iron or impurity by other minerals. It is not specifically deemed dangerous and is classified as irritant dust in powder form. Two types of talc: industrial and cosmetic, are used in paper plastics, rubber, paint, and cosmetic manufacturing work. The cosmetic powder is packaged as a compact powder or a loose powder, which is used for makeup and contains heavy metals such as Cd, Co, Pb, Cu, and Cr. A study on thirty different brands of talcum powder showed that metals are present in safe limits, but the excess use of talcum powder affects the health of the consumer. And there are articles in the literature that conclude that talc is not harmful through selected area electron diffraction combined with energy dispersive X- ray analysis found that Pinerolo Italian cosmetic talc does not cause any cancer risk, which is due to its purity. Similarly, French and Austrian talc workers were examined for the effects of talc dust on the respiratory system using pulmonary function tests and chest X- ray, but neither showed any evidence of detrimental effects of talc exposure. Talc is used in the treatment of idiopathic spontaneous pneumothorax although it might result in mild restrictive impairment of lung function and pleural thickening as seen in the chest X- ray [9].

### **2.9.2 Crayon formulation**

The process by which the paraffin-based crayons are made includes mixing stearic acid and pigments with paraffin heated to 160 °F Once mixed, and further heated to 20-250 °F the molten solution is added to molds. When cooled, the crayons are removed from molds and packaged [10].

Another approach for crayon production consists of the following ingredients, combined in the proportions stated: Carnauba-Wax, one pound; Stearic acid, one pound; paraffin-Wax, one and one-fourth pound, and sufficient coloring-pigment to give to the mixture the desired color. These

ingredients, in about the proportions mentioned, are melted and mixed and the melted mixture is poured into molds. The mixture hardens directly upon being poured into the molds.

The employment of the carnauba-wax renders the crayon hard. The stearic acid softens the carnauba-wax, which is naturally very hard. The carnauba - wax and stearic acid mixed alone will give a slight mark. The addition of the paraffine somewhat softens the mixture of the stearic acid and carnauba-Wax and enables the crayon composed of the mixture to make a better and heavier mark. The carnauba-wax and the paraffine in the mixture toughen the crayon and prevent it from becoming soft in a warm atmosphere or from the heat of the hand. This softening of the crayon in crayons made with wax is a great objection heretofore, Quantities of crayon in stock softening in a warm atmosphere. This crayon is said to be equally efficacious in marking coarse and fine fabrics and may be used on all kinds of materials [59].

Crayon wax composition consists essentially of the paraffin wax in the amount of about 30%-95% by weight, the microcrystalline wax in the amount of about 1%-5% by weight, the stearic acid in the amount of about 10%-50% by weight, and the pigment in the amount of about 0.5%-25% by weight [60]. crayon wax composition comprising a base wax, stearic acid, and a pigment wherein the wax base is paraffin wax and is in the amount of from about 50% to about 90% by weight of the composition, the stearic acid is in the amount of from about 25% to 35% by weight of the composition and the pigment is in the amount [59]. Modern crayons are a combination of pigment and wax that is paraffin wax (9g), beeswax (5g), stearic acid (0.5g), and pigments (0.25g) [1]. And the stearic acid is used to make cosmetic and personal care items such as soap, lotions, and creams. Figure 2.4 below show the chemical structure of stearic acid.

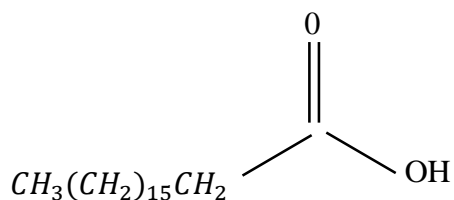


Figure 1 2.4: chemical structure of stearic acid.

The composition of crayon formulation is paraffin wax, stearic acid, talc, and pigments [61]. Stearic acid is used for lubricant and gives moisturizing product, talc is used to absorb moisture, help to cut down on friction and improve the feel of the product, paraffin wax used improve

breaking quality, resistance breaking and marking to the crayon wax, and pigment or dye is used for coloring purpose.

### **2.9.3 Application of crayon**

Crayon, as used for refers to a stick of wax composition, preferably colored, used for drawing, and The process for making permanent fabric marking crayons of the present invention includes blending a mixture of wax, stearic acid, and a triglyceride-containing mixture is used for coloring purpose [10]. The students used crayons for dawning artists and at the school level also used for drawing. A conventional crayon was used since the late 1790s as a drawing crayon for artists [1].

## CHAPTER THREE

### 3. MATERIAL AND METHODS

#### 3.1 Materials and Equipment

Equipment and material used in this case were a knife, oven, desiccator, grinder, screen sieve, weight balances, gloves, Petri dish, beaker, heater, aluminum foil, soxhlet extractor, chiller, rotary evaporator, condenser, bottom flask, extraction thimbles, heating plat, magnetic stirrer, UV-visible spectrophotometer, FTIR, TGA, and Tensile strength test.

The materials and reagents used in this study were; rumex abyssinicus, paraffin wax, beeswax, talc, stearic acid, and ethanol (99.5%).

#### 3.2 Preparation Procedure

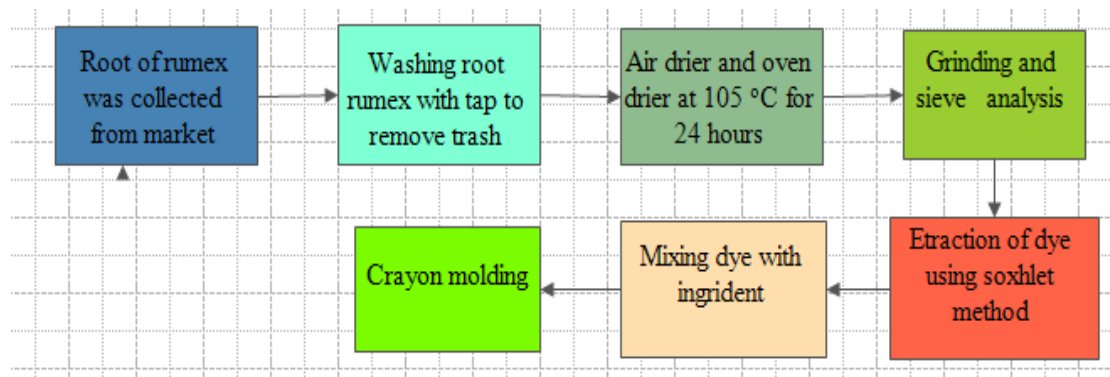


Figure 3.1: Framework of the experimental extraction of dye

Figure 3.1 showed the framework of crayon formulation using organic dye extracted from the root of rumex abyssinicus and mixing with ingredients of ( paraffin wax, talc, bee wax, stearic acid, and dye ), and then crayon was mold.

Root rumex samples were carefully washed with water, air-dried under the shade at room temperature, ground using an electric grinder, and screened. Conventional solid-liquid aqueous

extraction (1:10 g/l). The obtained aqueous extract was filtered by using a cotton cloth and concentrated to 20–25% solids [5].

- **Raw material collection**

The sample root of *Rumex abyssinicus* was purchased from a local market, which was collected from Asalla part of Ethiopia and was used for the dyeing experiments.

- **Raw material preparation**

Preparation of the root included cutting the cleaned root into small pieces, air-dried for 48hr and oven-dried at 105°C for 24hours.

The moisture removal from organic compounds that contain much amount of water in their content was best to dry in the oven at a range of temperature from 100°C to 105°C [62]

- Washing and cleaning

Cleaning or washing the root with tap water was the first process of preparation to remove the mud that comes with the root. Also, cleaning of the root was used for removing other unwanted materials.

Root samples were carefully washed with water and

- Peeling

After cleaning the cover of the root was peeled by a knife.

- Cutting

The peeled root was cut to make it suitable for the next drying step by a knife.

- Drying

The root was left to dry in oven-dried at 105°C for 24hours.

- Grinding

After drying the size was further reduced particle size (0.355mm to 0.71mm) by using a ball mill for better dye extraction efficiency.

This particular size range was selected because literature revealed that to have a higher yield of extracted product was high at small particle size. After all, large particle size has a small surface area, and it's difficult to entrance solvent, the range of particle size (0.355 to 0.5mm) was given high yield [62].

- **Extraction method**

- Solvent Extraction

The extraction was done by using an apparatus called soxhlet which is used for many extraction purposes in the laboratory using different solvents, such as n-hexane, ethanol, methanol, which was ethanol in this study.

### **Experimental procedure**

- An empty and clean thimble was weighed and recorded
- The thimble that containing the sample of sieved size (0.355mm-0.71mm) was then weighed again and the value was recorded. The sample in the thimble was subsequently covered and put in an extraction chamber; the dried ground samples were prepared to the volume of ethanol ratio of (0.05g/ml, 0.075g/ml, and 0.1g/ml) which is suspended above a flask containing the solvent and below a condenser and ethanol was measured and poured into a round-bottomed flask.
- The extraction chamber was mounted on this flask and fixed under the condenser, which is already clamped to a retort stand. Besides, the condenser was already connected to two pipes, one pipe connected to a water supply (tap) and the other removes water from the condenser.
- The electro thermal heating mantle was switched on and the temperature was set at 78°C, since the solvent used for extraction was ethanol and the boiling point of ethanol was 78°C.
- The flask was heated and the solvent evaporated and move up into the condenser where it is converted into a liquid that trickles into the extraction chamber containing the sample.
- The extraction chamber is designed so that when the solvent surrounding the sample exceeds a certain level it overflows and trickles back down into the boiling flask.
- At the end of the extraction process, which lasts in time (1.5h, 3.25h, and 5h), the heating mantle was switched off and the flask containing the solvent and extracted dye was removed. And separated by rotary evaporator

Dye was extracted from orange peel by using the soxhlet extraction method and the dried ground samples were prepared together to the volume of ethanol ratio (0.05g/ml, 0.075g/ml, and 0.1g/ml) and time (1.5h, 3.25h, and 5h) [4].



(a)



(b)



(c)

Figure 3.2: Rumex abyssinicus preparation process: raw material was collected (a), washed (b), and grinding (c).

Figure (3.2) showed the process of preparing raw material for purpose of extraction dye from rumex abyssinicus.

### **3.3 Characterization of rumex abyssinicus (mekmeko)**

#### **3.3.1 Determination of Moisture Content**

Moisture content was determined after oven drying to a constant weight at 105°C, the method was based on drying a sample in an oven and determining moisture content by the weight

difference between dry and wet material. At the end of the 24hours, the crucible plus sample was removed from the oven and transferred to the desiccator, and weighed [63].

22.5g of the cleaned air-dried root of rumex was taken in a crucible and dried in an oven at a temperature of 105°C for 24hours and the weight was taken after every 2hours. The procedure was repeated until a constant weight was obtained. After every 2hours, 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:

$$\text{Moisture content (\%)} = \frac{w_1 - w_2}{w_2} * 100 \dots\dots\dots (1)$$

Where,  $w_1$  = is the original weight of the sample taken

$w_2$  = is the weight of the sample after drying

### 3.3.2 Determination of Ash Content

A dry crucible containing 22.5g of an oven-dried sample of the root of rumex was placed in a muffle furnace set at 550°C for 3hours and the sample was cooled in a desiccator for 30minute and weighed on an analytical balance. The ash contents were analyzed according to Associates of Analytical Chemistry (AOAC) methods [32]. The (%) of ash content was calculated using the following formula:

$$\text{Ash content (\%)} = \frac{w_1}{w_2} * 100 \dots\dots\dots (2)$$

Where,  $w_1$  = weight of sample residue after ignition (g)

$w_2$  = weight of dry sample taken (g)

### 3.3.3 Determination of volatile organic compound

The dried sample after moisture removal was taken in a crucible and placed in an electrically heated in muffle furnace at a temperature of 920°C for 10minutes and then cooled in desiccators for 30minutes. It was then removed and re-weighed. The percentage of weight loss gave the volatile matter content [64]. The weight of 22.5g dried rumex moisture removal was taken in a crucible and the weight of volatile matter on a dry basis of the sample was determined as the difference between the dry weight of samples and the weight of the sample residue after ignition.

$$\text{Volatile matter (\%)} = \frac{w_2 - w_1}{w_2} \dots\dots\dots (3)$$

Where,  $w_1$  = weight of sample residue after ignition (g)

$w_2$  = weight of dry sample taken (g)

### 3.4 Experimental design and optimization of dye

Data analysis was carried out by DESIGN EXPERT 11.1.0.1 software. Software design is used to evaluate the effects of the process variables. Optimal conditions for dye extraction were studied based on the Response Surface Methodology (RSM). In this investigation, the natural dye was extracted using the soxhlet extraction method and a three-variable design for RSM was used to develop a statistical model to describe the yield of natural dye from the root of rumex.

Significance within and between extractions was set from analysis of variance (ANOVA) at P-value  $\leq 0.05$ .

RSM was used to optimize the extraction of natural dyes from the root of rumex. Design expert was used in the optimization of process variables with three factors at three levels. 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 were obtained by numerical optimization based on the partitioned into linear, quadratic, and interactive components.

### 3.5 Dye determination

The natural dye extract was concentrated by using a rotary evaporator at 45°C and 250rpm (appendix B). The dried extract was collected, stored in a desiccator, and used for estimation of the percent dye yield by applying the following formula [4].

$$\text{Yield (\%)} = \frac{\text{weight of dye extracted}}{\text{weight of sample used}} * 100 \dots\dots\dots (4)$$

Table (3.1) showed the experimental design used for extraction of dye from the root of rumex abyssinicus by using variables of (particle size, solid-liquid ratio, and time) and maximum yield was selected for characterization and crayon formulation.

Table 3.1: Experimental Design for optimization of dye

Std	Run	Sieve size (mm)	Ratio(sol/liq) (g/ml)	Time (hr)	Yield (%)
27	1	0.355	0.1	5	
6	2	0.355	0.075	1.5	
8	3	0.5325	0.1	1.5	
25	4	0.71	0.1	5	
3	5	0.355	0.05	1.5	
2	6	0.5325	0.05	1.5	
4	7	0.71	0.075	1.5	
12	8	0.355	0.05	3.25	
17	9	0.5325	0.1	3.25	
26	10	0.5325	0.1	5	
14	11	0.5325	0.075	3.35	
18	12	0.355	0.1	3.25	
7	13	0.71	0,1	1.5	
15	14	0.355	0.075	3.25	
24	15	0.355	0.075	5	
10	16	0.71	0.05	3.25	
21	17	0.355	0.05	5	
20	18	0.532	0.05	5	
11	19	0.5325	0.05	3.25	
9	20	0.355	0.1	1.5	
13	21	0.71	0.075	3.25	
16	22	0.71	0.1	3.25	
19	23	0.71	0.05	5	

22	24	0.71	0.075	5	
23	25	0.5325	0.075	5	
5	26	0.5325	0.075	1.5	
1	27	0.71	0.05	1.5	

## 3.6 Characterization of dyes

### 3.6.1. Double beam UV-vis spectrophotometer

Ultraviolet (UV) and Visible (VIS) spectrophotometry (SM-1600 Spectrophotometer) has developed the technique of selection in most laboratories concerned with the identification and quantification of organic and inorganic compounds through a varied range of products and processes. Modern spectrophotometers were quick, accurate, and reliable. UV-Vis spectroscopy was a technique for determining absorbance as a function of the wavelength of dye extracted from the root of rumex scan from 200 to 600nm. A sample is irradiated with an intensity of UV-vis light and the intensity after the sample was measured [4]. A scan from 200 to 600nm was performed to generate the characteristic absorption spectra of the dye [65]. Uv-vis spectrophotometer measures the intensity of light passing through a liquid sample (i.e. dye solution) at different wavelengths and guesses the maximum wavelength that gives the highest absorbance.

### 3.6.2 Fourier transforms infrared spectroscopy (FTIR) spectroscopy

Infrared spectroscopy was an important and critical characterization method to explain the structure of matter at the molecular scale. The chemical composition and the bonding organization of ingredients in a homo-polymer, copolymer, and polymeric materials in common can be achieved using Infrared (IR) spectroscopy the wavelength number was  $4000\text{-}400\text{cm}^{-1}$ . The FTIR spectrometers achieve 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. Statistical Fourier analysis provides the relation of intensity and frequency that was the IR spectrum. For analysis of the chemical composition of dye extracted from orange peel, the wavelength number was  $4000\text{-}400\text{cm}^{-1}$  [4].

### 3.7 Mixing of raw material analysis

paraffin wax was measured from ( 4g to 8g) and melted at a temperature (47°C-68°C), the beeswax that was measured (1g) and beeswax were melted at a temperature between (63°C and 65°C) on a magnetic stirrer (85.2 model) and properly mixed, then fine powder of talc (5g to 9g) was added, and 0.5g of stearic acid melted at 69.3°C was added to the mixing and they stirred, then after the stirred ensure properly mix the dye (0.5g to 2g) was also added at the magnetic stirrer temperature was runs (80°C, 90°C and 100°C) and time of mixer were started from (2 minutes to 3minutes) through different experiments runs. The composition of ingredients used for crayon formation was paraffin wax, stearic acid, filler (talc), and pigments [61] and Crayons have historically contained a predominant concentration of paraffin, a wax such as Bee's wax or Carnauba wax, stearic acid, and a non-toxic pigment to impart color, crayons were made includes mixing stearic acid and pigments with paraffin heated to 160 °F (71°C) and were then added and the mixture was placed on an electric hot plate at 210 F (98 °C ) and stirring for 2 to 3minutes [10].

### 3.8 Experimental design and optimization of crayon

DESIGN EXPERT 11.1.0.1 software was used to evaluate the effects of the process variables and investigates the optimum parameters (paraffin wax, talc, dye mixing, and temperature) for the optimization product. Linear regression analysis was applied to investigate the relationship between a dependent variable and the independent variable. The analysis was determined by using design expert or analysis of variance (ANOVA) would be carried out to sort out the effect as a result of using different conditions, and to understand the main and the interaction effects. The response of crayon formulated used for coloring was determined by using UV- Vis spectra, by the major absorption maxima and maximum wavelength that gave maximum absorption ( $\lambda_{max}$ ) was recorded to determine the absorption crayon in the region scan from 200nm to 700nm. The absorbance of a solution of the coloring matter is determined at its wavelength of maximum absorption ( $\lambda_{max}$ ) and measurement of absorbance in the region was scan from 200nm to 70nm was performed to generate the characteristic absorption spectra [66].

Table (3.2) below showed the optimization of crayon formulated depend on the absorbance of spectra by using process variable: paraffin wax (4g to 8g), dye (0.5g to 2g), talc (5g to 9g), and

temperature of magnetic stirrer (80°C to 100°C) and also at a constant value of stearic acid 0.5g and bee wax 1g. The selected process variable for optimization was which has a major effect on the formulation of crayon during preliminary work.

Table 3.2: Experimental Design for optimization of crayon

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	Run	A:Talc	B:Dye	C:Paraffin wax	D:Temperature	absorbance
		g	g	g	°C	
3	1	5	2	6	90	
21	2	7	0.5	6	80	
22	3	7	2	6	80	
14	4	7	2	4	90	
15	5	7	0.5	8	90	
13	6	7	0.5	4	90	
4	7	9	2	6	90	
9	8	5	1.25	6	80	
1	9	5	0.5	6	90	
5	10	7	1.25	4	80	
7	11	7	1.25	4	100	
17	12	5	1.25	4	90	
24	13	7	2	6	100	
2	14	9	0.5	6	90	
11	15	5	1.25	6	100	
8	16	7	1.25	8	100	
10	17	9	1.25	6	80	
19	18	5	1.25	8	90	
23	19	7	0.5	6	100	
6	20	7	1.25	8	80	
16	21	7	2	8	90	
20	22	9	1.25	8	90	

12	23	9	1.25	6	100	
18	24	9	1.25	4	90	

### 3.9 Characterization and mold of crayon formulated

Characterization of crayon that was obtained at the optimum point and comparing with commercial crayon and mold formulated crayon. The dimension of crayon mold was diameter versus height (1cm diameter cm \*8.5cm height), which was the demission of commercial crayon.

#### 3.9.1 Double beam UV-vis spectrophotometer

In this study, UV- Vis spectra (SM-1600 Spectrophotometer) were used for the optimization of crayons by using absorbance as the response. And also used for characterization of optimized crayon and market crayon by comparing absorbance as a function of wavelength for optimized crayon and commercial crayon in the region scan from 200nm to 700nm. The absorbance of a solution of the coloring matter is determined at its wavelength of maximum absorption ( $\lambda_{max}$ ) and measurement of absorbance in the region was scan from 200nm to 700nm [66].

#### 3.9.2 Fourier transform infrared spectroscopy (FTIR) spectroscopy

Fourier Transform Infrared Spectrometer (FTIR) is an analytical technique used to identify organic, polymeric, and, in some cases, inorganic materials. In addition to that, it's studying the change of the functional groups of crayon formulated. FTIR spectroscopy analysis for crayon formulated from ingredients (paraffin wax, talc dye, stearic acid, and beeswax) showed the chemical composition and the bonding organization of ingredients in a homo-polymer, copolymer, and polymeric materials in common can be achieved in the crayon product using Infrared (IR) spectroscopy, the range of wavelength  $4000-400cm^{-1}$ . For analysis of the chemical composition, the wavelength number was  $4000-400cm^{-1}$  [62].

#### 3.9.3 Thermogravimetric Analysis (TGA)

TGA is a thermal analyzer that displays the mass of the sample versus temperature. TGA thermograms were showing the weight loss and derivative weight loss versus the temperature range from standard (25°C ) to temperature to 700°C for crayon and commercial crayon. It also provides good information that can be used to forecast the lifetime of materials, select materials for certain end-use applications, forecast product performance, and develop product quality and

thermal stability. For the thermogravimetric analysis to be carried out, a small amount of the sample (22-30mg) was placed in a vial, which was present in the TGA analyzer (SDT Q600 V20.9 Build 200) instrument.

The thermal degradation of the isolated compounds occurs with a degradation peak of colorant was showing the weight loss and versus the temperature the range from standard 25°C to temperature to 700°C [18].

### 3.9.4 Tensile Strength test

The tensile strength of the composites was measured on a tensile testing machine the maximum continuously applied load has divided by the cross-sectional area of the film. Tensile strength is defined as the strength of a material in terms of force per unit area of cross-section while applying force in the linear direction [67].

$$\text{Tensile strength} = \frac{\text{Force (N)}}{\text{Area (Width in mm x Thickness in mm)}} \dots\dots\dots (6)$$

In this study kind of test was a tensile test in figure (3.33) (WP 310 universal material tester 50KN) below which was test tensile strength of crayon and It is the load per unit area of cross-section required to pull apart or break a strip of crayon, dimensions of specimen 10mm (1cm) diameter with 85mm (8.5cm) height of a sample of formulated crayon and commercial crayon was a display to determine tensile strength and tensile break test by considering tensile stress versus Percentage Elongation at break (%).

As the films break, the distance between the two grips was measured and the maximum forces were taken. It can be obtained by dividing the difference of initial and final specimen length to the initial grip separation length and multiplying the result by hundred. Percent elongation at a breakpoint is calculated by the following formula;

$$\text{Percentage of strain (\%)} = \frac{\text{final length at break} - \text{initial length}}{\text{initial length}} \dots\dots\dots (7)$$

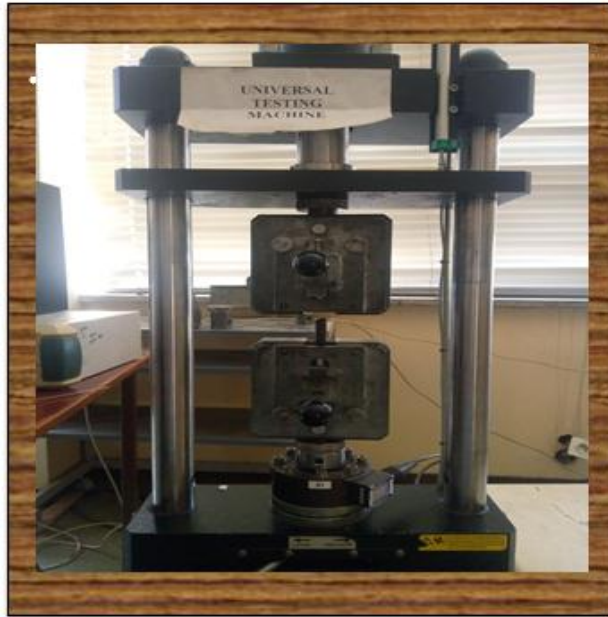


Figure 3.3: Tensile testing equipment (WP 310 universal material tester 50KN)

### **3.9.5 Binding and Durability test**

binding of color was express the color formulated crayon for drawing was binding on the material or not by considering the visibility of color on the material was how it's binding. And Durability of color was determined by using sunlight at a standard temperature applying colored material on the sunlight for 7day, without sunlight (in the room) for 7days, and an oven at 50°C for 2days to considering temperature difference to refer to the durability of color on the material and its compared with the binding color of commercial crayon on the material. And the digital camera was used to show the pictures of colored material (appendix C). Test specimen's durability of color on the matter was made keeping in ordinary temperature difference for compression [68].

## CHAPTER 4

### 4. Result and Discussion

#### 4.1 proximate analyses of Rumex Abyssinicus (Mekmeko)

(Table 4.1) the blow was showing the proximate analyses of rumex abyssinicus: moisture content, ash content, and a volatile organic compound.

Table 4.1: proximate analyses of Rumex Abyssinicus

parameters	Average value
Moisture Content (%)	6.007
Ash Content (%)	4.66
Volatile organic compound (%)	24.4

#### 4.2 Experimental design for optimization yield of dye

Table (4.2) shows the result of the 27 experiment runs carried out according to response surface design. 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: Summary of build information for design layout

File Version	11.1.2.0		
Study Type	Response Surface	Subtype	Randomized
Design Type	3 Level Factorial	Runs	27
Design Model	Quadratic	Blocks	No Blocks
Build Time (ms)	2.00		

The natural dye extracted from rumex abyssinicus (different amount of rumex abyssinicus was prepared for every 27 experimental runs ) and the yield of dye extracted from Rumex Abyssinicus at experimental condition (extraction time, particle sizes, and rumex abyssinicus to ethanol ratio) were calculated by determining the response of maximum yield in Table (4.3) according to equation (1).

Table 4.3: Experimental design layout for extraction of dye from rumex abyssinicus

		Factor 1	Factor 2	Factor 3	Response 1
Std	Run	A:particle size (mm)	B:ratio(sol/liq) (g/ml)	C:time (hr)	Yield (%)
27	1	0.355	0.1	5	0.47
6	2	0.355	0.075	1.5	0
8	3	0.5325	0.1	1.5	0
25	4	0.71	0.1	5	0.35
3	5	0.355	0.05	1.5	0
2	6	0.5325	0.05	1.5	0
4	7	0.71	0.075	1.5	0
12	8	0.355	0.05	3.25	0.27
17	9	0.5325	0.1	3.25	0.22
26	10	0.5325	0.1	5	0.4
14	11	0.5325	0.075	3.25	0.24
18	12	0.355	0.1	3.25	0.29
7	13	0.71	0.1	1.5	0
15	14	0.355	0.075	3.25	0.32
24	15	0.355	0.075	5	0.53
10	16	0.71	0.05	3.25	0.15
21	17	0.355	0.05	5	0.45
20	18	0.5325	0.05	5	0.38
11	19	0.5325	0.05	3.25	0.21
9	20	0.355	0.1	1.5	0
13	21	0.71	0.075	3.25	0.18

16	22	0.71	0.1	3.25	0.13
19	23	0.71	0.05	5	0.34
22	24	0.71	0.075	5	0.36
23	25	0.5325	0.075	5	0.42
5	26	0.5325	0.075	1.5	0
1	27	0.71	0.05	1.5	0

The maximum percentage dye yield obtained was 0.53% at particle size 0.355mm, extraction time 5hour and rumex abyssinicus to ethanol ratio 0.075 g/ml respectively whereas the minimum percent dye yield was 0 which occurred in nine of the twenty-seven experiments. These least outputs were observed at particle size (0.71, 0.53, and 0.355)mm, extraction time 1.5hour and rumex abyssinicus to volume of ethanol ratio (0.1, 0.075, and 0.05)g/ml.

The maximum yield of natural dye extracted from orange peel was obtained (0.40%) at orange peel to the volume of ethanol ratio 0.075mm and extraction time 5hour [4].

### 4.3 Determination of dye extracted from rumex abyssinicus

Figure (4.1) below was showing the yield of dye extracted from rumex abyssinicus at the optimum point of the variable studied. The dye extracted from rumex abyssinicus through different run and the yield of dye extracted was show below at selected point of parameters.



Figure 4.1: extracted dye from Rumex abyssinicus

## 4.4 Statistical model equation

### 4.4.1 Analysis of ANOVA for the quadratic model

The analysis of variance (ANOVA) obtained from design expert software, which tells us the significance of different factors

Table 4.4: Analysis of variance (ANOVA) for Response Surface of percentage dye yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.8175	9	0.0908	171.33	< 0.0001	significant
A-particle size	0.0374	1	0.0374	70.46	< 0.0001	
B-Ratio(sol/liq)	0.0002	1	0.0002	0.3772	0.5472	
C-time	0.7606	1	0.7606	1434.54	< 0.0001	
AB	0.0002	1	0.0002	0.3930	0.5391	
AC	0.0133	1	0.0133	25.15	0.0001	
BC	0.0002	1	0.0002	0.3930	0.5391	
A <sup>2</sup>	0.0002	1	0.0002	0.3493	0.5623	
B <sup>2</sup>	0.0036	1	0.0036	6.76	0.0187	
C <sup>2</sup>	0.0019	1	0.0019	3.58	0.0758	
Residual	0.0090	17	0.0005			
Lack of fit	0.004	8	0.0041	0.81	0.42	not significant
Pure error	0.0051	6	0.0046			
Cor Total	0.8265	26				

The Model F-value of 171.33 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. “F” test with a very low probability value [(P-model > F) < 0.0001].

P-values less than 0.0500 indicate model terms are significant. In this case, A, C, AC, B<sup>2</sup> 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.

In this case, A-particle size, C-Extraction time, AC- interaction factor of particle size and time, and B-pure quadratic were significant model terms.

Design-expert was applied to analyze results on the extraction process and a second-order polynomial equation with the interaction terms was derived to express the extraction dye and the final model equation in terms of a coded factor was presented by equations representing the variation of percentage dye yield of Rumex Abyssinicus with independent factors.

Final Equation in Terms of Coded Factors:

$$\text{Yield} = -0.2359 - 0.0456A + 0.0033B + 0.2056C + 0.0042AB + 0.0333AC + 0.0042BC + 0.0056A^2 + 0.0244B^2 - 0.0178C^2 \dots\dots\dots 4.1$$

The equation 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 extracted from Rumex was affected by terms of particle size (A), rumex abyssinicus to the volume of ethanol ratio (B), extraction of time (C), pure quadratic terms (A<sup>2</sup>, B<sup>2</sup>, and C<sup>2</sup>) and interaction quadratic terms (AB, AC, and BC).

It was noted that yield of dye increase with increase rumex abyssinicus to the volume of ethanol ratio (B) and extraction of time (C) which were a positive linear effect on the yield of dye and decrease with particle size (A). Pure quadratic term (A<sup>2</sup>) was a positive effect on the yield of dye response, but the pure quadratic terms (B<sup>2</sup> and C<sup>2</sup>) were a negative effect on the yield of dye response.

The interaction of interaction factor of particle size and time (AC), the interaction of factor of particle size and rumex abyssinicus to the volume of ethanol ratio (AB), and rumex abyssinicus

to the volume of ethanol ratio and extraction of time (BC) were positive effect on the yield of dye response.

Final Equation in Terms of Actual Factors

$$\text{Yield} = -0.277373 - 0.350324 \text{ sieve size} + 5.19048 \text{ ratio(sol/liq)} + 0.090907 \text{ time} \\ + 0.938967 \text{seive size} * \text{ratio(sol/liq)} + 0.107311 \text{ seive size} * \text{time} + 0.095238 \\ \text{ratio(sol/liq)} * \text{time} + 0.176332 \text{seivesize}^2 - 39.11111 \text{ratio(sol/liq)}^2 - 0.005805 \text{time} \dots \dots \dots 4.2$$

The equation (4.2) 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 4.5: Fit Statistics between predicted and adjusted value.

Std. Dev.	0.0230	R <sup>2</sup>	0.9891
Mean	0.2115	Adjusted R <sup>2</sup>	0.9833
C.V. %	10.89	Predicted R <sup>2</sup>	0.9697
		Adeq Precision	37.9413

The Predicted R<sup>2</sup> of 0.9697 is in reasonable agreement with the Adjusted R<sup>2</sup> of 0.9833; i.e. the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Your ratio of 37.941 indicates an adequate signal. This model can be used to navigate the design space. The regression coefficient R<sup>2</sup> was explaining the correlation between both the experimental data and the predicted responses.

The Results of term R<sup>2</sup> = 0.9891 and Adj R<sup>2</sup>= 0.9833 from Table 4-5 obtained reflect that the predicted values were found to be in good correlation with experimental values.

When the value of R<sup>2</sup> was an approach to 1.0 the regression line fits the data. According to the value of R<sup>2</sup> = 0.9891 from table 4.5 only 0.011 of the total variance was not defined by developed regression. The adjusted R<sup>2</sup> =0.9833 was also good for confirming the significance

model. The Predicted  $R^2 = 0.9697$  express the model will indicate a high percentage of the variability in new data.

Design-Expert® Software  
yield  
Color points by value of  
yield:  
0 0.53

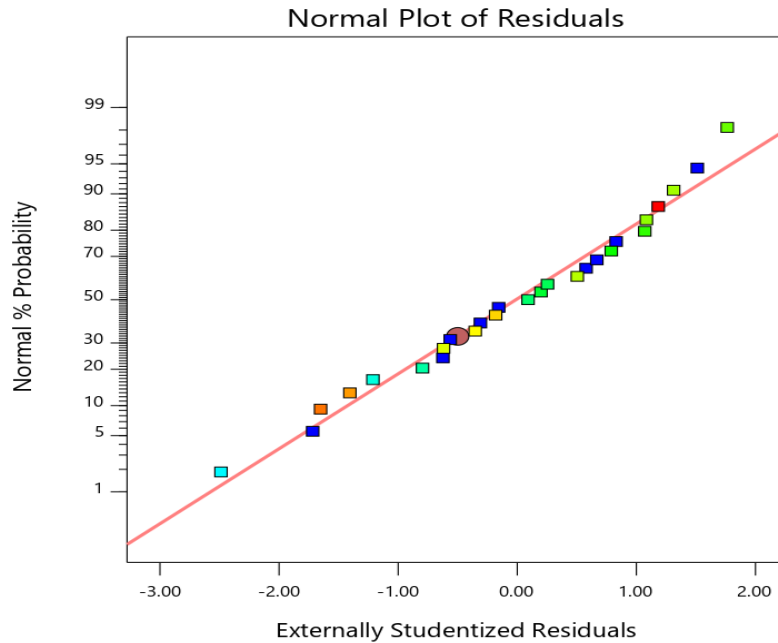


Figure 4.2: Normal plot of residuals

This normal probability plot expresses the residuals followed by the normal % probability and this experimental data graph indicates the plot was fitted to the straight line; this means the assumption of variance analysis was satisfied by the equation of the quadratic polynomial model. Therefore the distribution of error approximately the approach to normal.

yield

Color points by value of

yield:

0 0.53

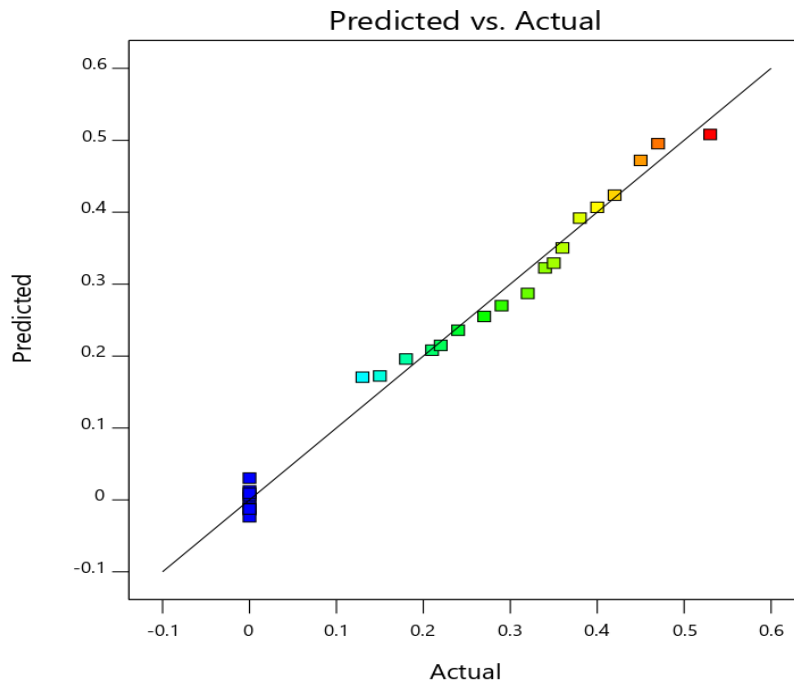


Figure 4.3: predicted versus actual value

This plot of predicted versus actual value indicates how the model is precisely done. From figure (4.3) the point expresses how the predicted value and actual value of each run was an approach to the straight line and the straight line showed how the predicted and actual value was an approach to each other. When the point above the straight line occurred, the predicted value was greater than the actual value, and when the point below the straight line occurred actual value was greater than the predicted value.

## 4.5 Effect of process parameters on the yield of dye

### 4.5.1 Effect of extraction time

The extraction time plays a great role in the percentage yield of dye extracted from rumex abyssinicus by using the soxhlet extraction method. There was a strong relationship between the soxhlet extraction methods and the yield of dye extracted at a time varies, but at a constant value of particle size and rumex abyssinicus to volume of ethanol ratio process parameters.

From figure (4.4) the yield of dye was correlated with the time of extraction, the yield of dye was increased as the time is increased. The extraction time run from lower level 1.5h to 5h higher

level as the yield of natural dye from rumex abyssinicus using the soxhlet extraction method was enhanced. At the constant value of particle size (0.5325mm) and rumex to ethanol ratio (0.075g/ml) the yield was changed from the table (4.3) regarding time changed, the yield was (0 %) at time 1.5hr, the yield was (0.24%) at time 3.25hr and yield was (0.42%) at time 5hr. The yield of dye extracted increased as time increased means increasing the time role in soxhlet extraction to longer contact between the rumex abyssinicus (raw material) and soxhlet extraction. due to this case they produce a large amount of mass transfer.

In general, the rate of extraction of dye was high at the extraction of time was increased, but get slow gradually by the time when it's more than needed [4].

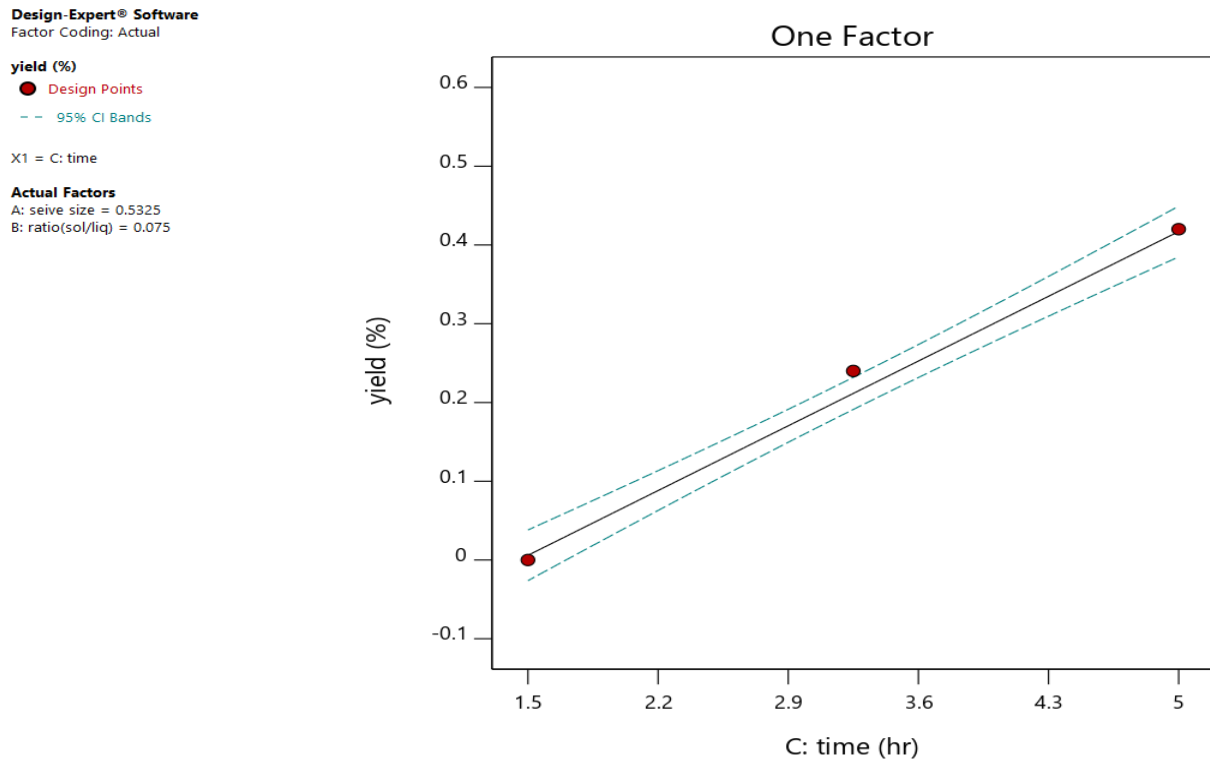


Figure 4.4: Effect of extraction time on the yield of dye

#### 4.5.2 Effect of rumex abyssinicus to volume of ethanol ratio on the yield of dye

Figure (4.5) shows the yield of dye was changed when rumex abyssinicus to volume of ethanol ratio changed from 0.05g/ml to 0.1g/ml at a constant value of time of extraction (3.25hr) and particle size (0.5325mm) according to the graph and the yield of dye fluctuated (Table 4.3). The plot shows that the effect of the rumex abyssinicus to volume of ethanol on the yield of dye was

(0.21%) at rumex to ethanol ratio 0.05 g/ml, the yield was (0.24%) at rumex to ethanol ratio 0.075g/ml and yield was (0.22%) at rumex to ethanol ratio 0.1g/ml. the maximum yield was obtained at particle size 0.075g/ml and the value of yield of dye was an approach to each other, this showed the effect of rumex abyssinicus to volume of ethanol ratio on the yield of dye was small. This was showed the grind rumex by a varying gram of rumex that used for extraction dye was already similar, because due to using the similar solvent extraction method (ethanol) used for extraction the effect of rumex to ethanol ratio was small.

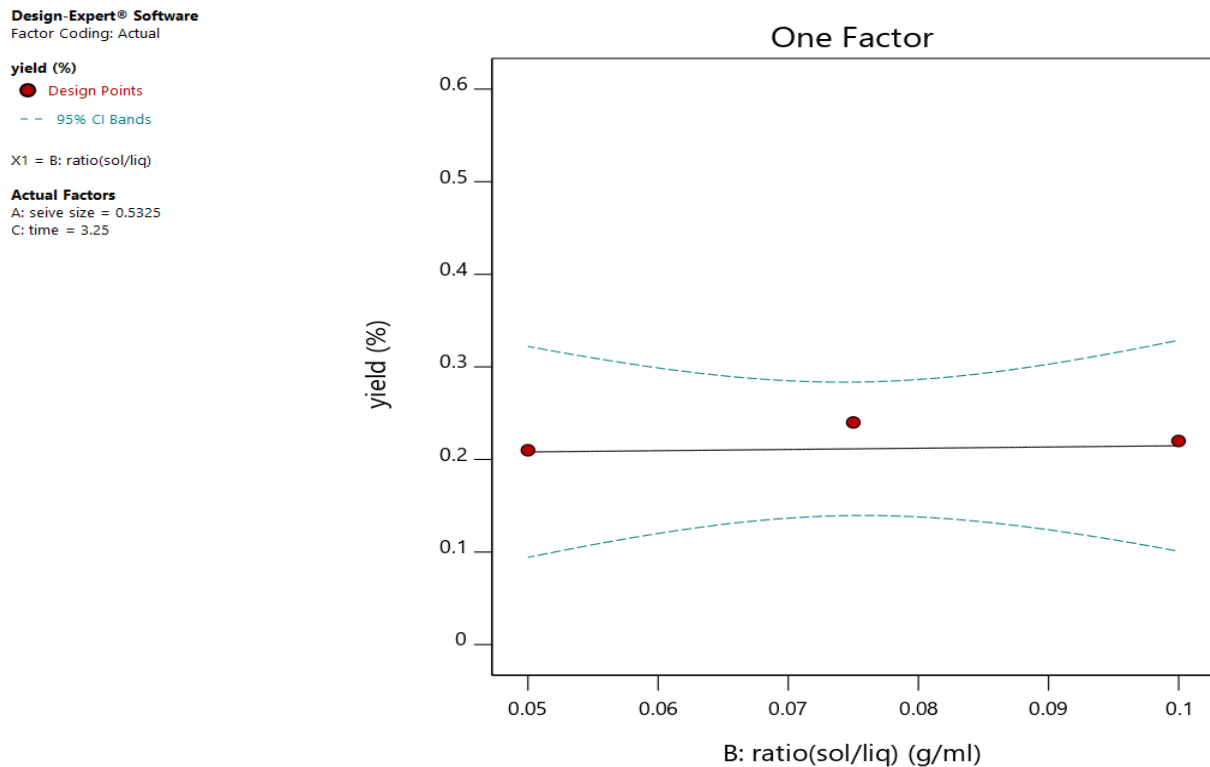


Figure 4.5: effects of rumex abyssinicus to volume of ethanol ratio on the yield of dye

#### 4.5.3 Effect of particle size on the percentage of yield of dye

Particle size also had a role in the yield of dye extracted from rumex abyssinicus (figure 4.6). From the graph, the percentage of yield of dye was oppositely related with particle size changed from (0.35mm to 0.71mm) at a fixed value of extraction time (3.25hr) and rumex to ethanol ratio (0.075g/ml), when smaller size gives high yield while larger particle size results from a lower yield, the yield was (0.32%) at particle size 0.355mm, the yield was (0.24%) at particle size 0.5325mm and yield was (0.18%) at particle size 0.18mm. This shows as the yield of dye was increased the particle size was decreased and less yield of dye was extracted from the larger

particle size. The reason is that bigger particles have a smaller surface area of contact and a larger distance to the solvent entrance and those bigger particles with smaller contact surface area have more resistance to the steam entrance and carried out and less mass transfer happened. During the soxhlet extraction method small particle size related to larger particle size, the small particle size was gives more yield than larger particle size, since larger particles have smaller contact surface area [32].

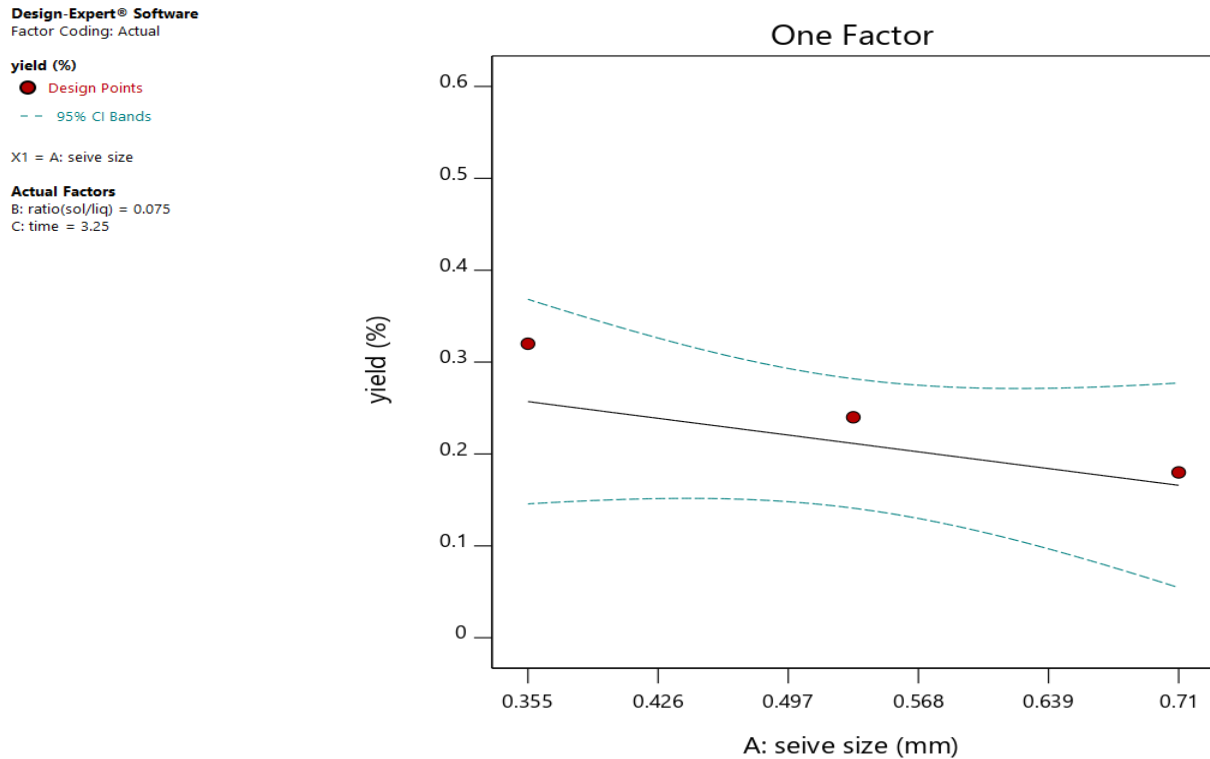


Figure 4.6: effect of particle size on the yield of dye

#### 4.6 Effect of interaction parameters on percent yield

The interaction response was further considerably affected by two interactive variables at constant third variable. Three dimensional (3D) response surface plots (plotted to recognize the interaction between the variables and the optimum level of each variable) and contours plots (presented the effect of two variables) were generated to regulate the optimum levels of the variables that were considered in this study. The plots were produced by keeping one variable fixed at the center point and changing the others within the experimental range. The resulting response surfaces displayed the effect of extraction particle size, extraction time, and rumex

abyssinicus to the volume of ethanol ratio on yield of dye. Therefore, in this case, three interaction factors were evaluated by the model equation.

AC- the interaction of particle size and time

AB- the interaction of particle size and rumex abyssinicus to volume of ethanol ratio

BC- Rumex Abyssinicus to volume of ethanol ratio and extraction of time

Therefore, the interaction factors with positive signs had a positive linear effect on the yield dye (as interaction factors increase the yield of dyes was also increased). Whereas, interaction factors with negative signs have a negative linear effect on the yield dye (as the interaction factors increase the yield of dyes was decreased).

#### **4.6.1 Effect of interaction of particle size and time on the yield of dye**

In figure (4.7) below shows that the Effect of interaction of particle size and time on the yield of dye at a constant value of rumex abyssinicus to volume of ethanol ratio (0.075g/ml), when time range from 1.5hr to 5hr and particle size( 0.355 to 0.71mm ). This figure (4.8) and table (4.3) indicates that the maximum yield of dye was achieved (0.53 %) at time 5hr and particle size range of (0.355mm) and the yield of dye was achieved at a different value of time and particle size. The yield of dye was (0%) at time 1.5hr and particle size range (0.71mm, 0.5253mm, and 0.33mm), the yield of dye was (0.18%) at time 3.25hr and particle size 0.71mm, the yield of dye was (0.24%) at time 3.25hr and particle size 0.5325mm, the yield was (0.32%) at time 3.25hr and particle size 0.355mm, the yield of dye was(0.36%) at time 5hr and particle size 0.71mm, the yield of dye was (0.42) at time 5hr and particle size 0.525mm and the yield of dye was (0.53%) at time 5hr and particle size 0.355mm. From this, it shows that when particle size was decreased yield of dye was increased. Figure 4.9 shows the response surface of 3D and counterplots developed in terms of the interaction of particle size and time. The yield of dye increased from 0% to 0.53% with the extraction of time 1.5hr to 5hr and particle size (0.71-0.355mm). But, upon increasing extraction time further than 5hr and particle size further than 0.355mm there was a decline of the yield of dye from 0.53% to 0.36% since the difficulty of purification happened due to the extraction of undesirable compounds.

Design-Expert® Software  
Factor Coding: Actual

yield (%)

● Design Points

-- 95% CI Bands

X1 = A: seive size

X2 = C: time

Actual Factor

B: ratio(sol/liq) = 0.075

C- 1.5

C+ 5

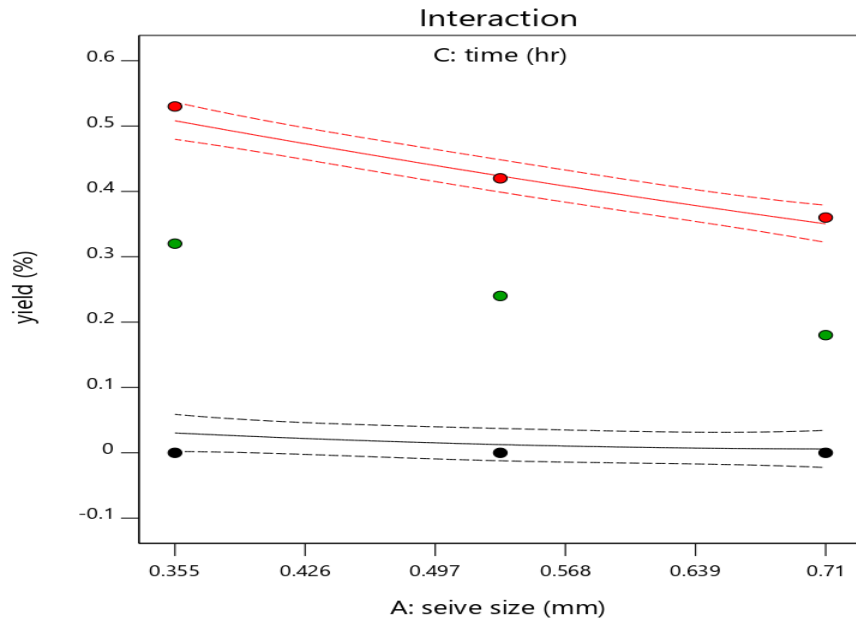


Figure 4.7: interactions of particle size and time on the yield of dye

Design-Expert® Software  
Factor Coding: Actual

yield (%)

● Design points above predicted value

○ Design points below predicted value

0 0.53

X1 = A: seive size

X2 = C: time

Actual Factor

B: ratio(sol/liq) = 0.075

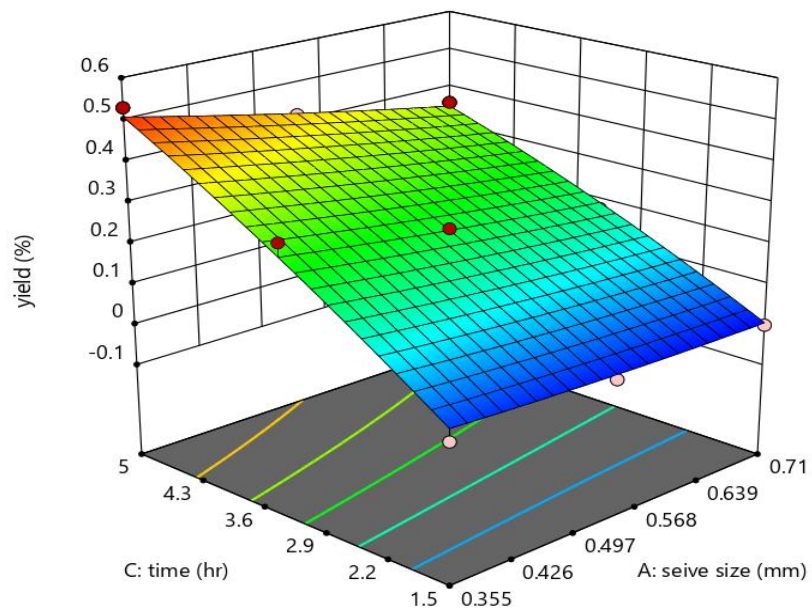


Figure 4.8: 3D and corresponding contour plot showing the effect of interactions of particles size and time on the yield of dye

#### 4.6.2 Effect of rumex abyssinicus to volume of ethanol ratio and extraction time

Figure (4.19) below shows that the Effect of interaction of rumex abyssinicus to volume of ethanol ratio and time on the yield of dye at a constant value of particle size (0.5325mm) at the center point. Figure (4.10) indicates that the yield of dye was achieved at a range of extraction and rumex abyssinicus to ethanol ratio. the yield of dye (0%) at time 1.5hr and rumex to ethanol ratio (0.05g/ml,0.075g/ml and 0.1g/ml), yield of dye was (0.21%) at time 3.25hr and rumex to ethanol ratio 0.05g/ml, yield of dye was (0.22%) at time 3.25hr and rumex to ethanol ratio 0.1g/ml, yield of dye was (0.24%) at time 3.25hr and rumex to ethanol ratio 0.0075g/ml, yield of dye was (0.38%) at time 5hr and rumex to ethanol ratio 0.05g/ml, yield of dye was (0.4%) at time 5hr and rumex to ethanol ratio 0.1g/ml and yield of dye was (0.42%) at time 5hr and rumex to ethanol ratio 0.075 g/ml. The maximum yield of dye (0.42%) was obtained at the extraction of time is 5hr and at rumex abyssinicus to volume of ethanol 0.075 g/ml. the yield of dye was increased as concerning the extraction of time increased and rumex abyssinicus to volume of ethanol ratio occurred at the middle, that was it is partial increased.

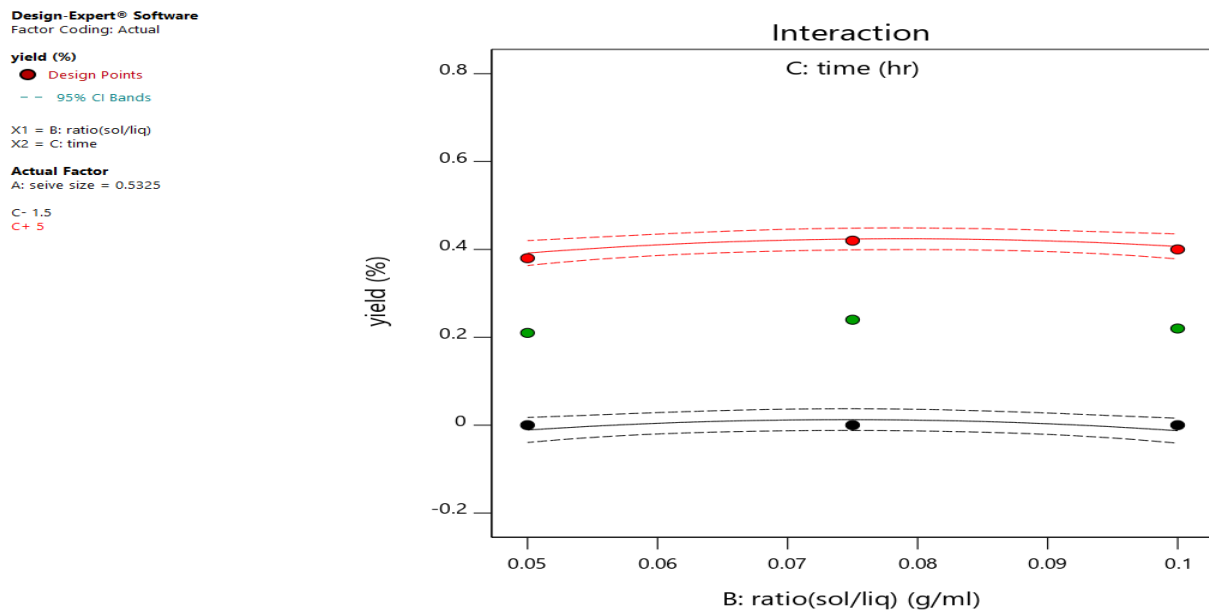


Figure 4.9: Rumex Abyssinicus to volume of ethanol ratio and extraction of time

yield (%)

● Design points above predicted value

○ Design points below predicted value

0 0.53

X1 = B: ratio(sol/liq)

X2 = C: time

Actual Factor

A: seive size = 0.5325

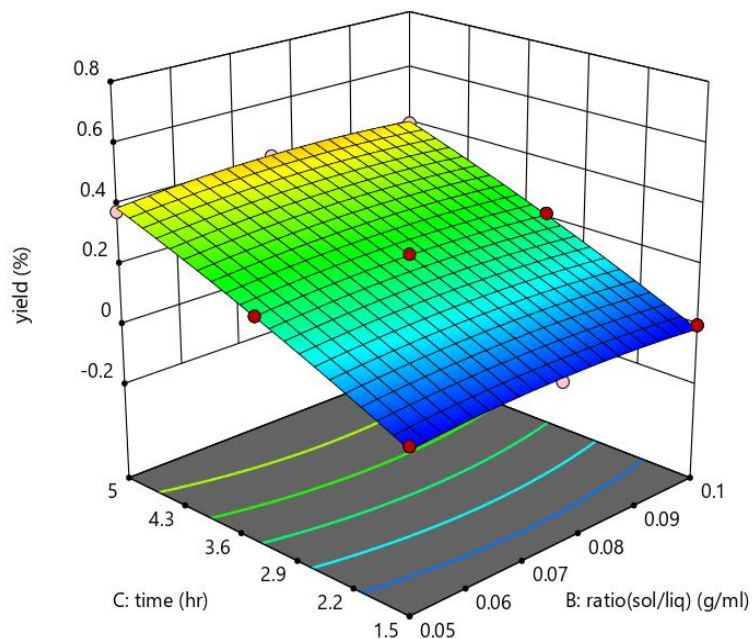


Figure 4.10: 3D and corresponding contour plot showing Rumex Abyssinicus to volume of ethanol ratio and extraction of time

#### 4.6.3 Effect of particle size and rumex abyssinicus to volume of ethanol ratio

Figure (4.11) below shows that the Effect of interaction of particle size and rumex abyssinicus to volume of ethanol ratio at a fixed value of time of extraction (3.25hr). Figure 4.12 and table (4.3) show that the yield of dye occurred at interval value of particle size and rumex to volume of ethanol ratio. The yield of dye was (0.13%) at particle size 0.71mm and rumex to ethanol ratio 0.1g/ml and the maximum yield of dye (0.32%) was obtained at particle size 0.355mm and at rumex abyssinicus to volume of ethanol 0.075g/ml. the yield increased as particle size decreased and rumex partial decreased by concerning the interaction of particle size and rumex abyssinicus to volume of ethanol ratio and they were more interacted. Figure (4.12) was shown the response surface of 3D and counterplots developed in terms of the interaction of particle size and rumex abyssinicus to volume of ethanol. From this figure, it was shown that the extraction of

natural dye was affected by the interaction of extraction particle size and rumex abyssinicus to volume of ethanol ratio since the lines in the plot were interacted.

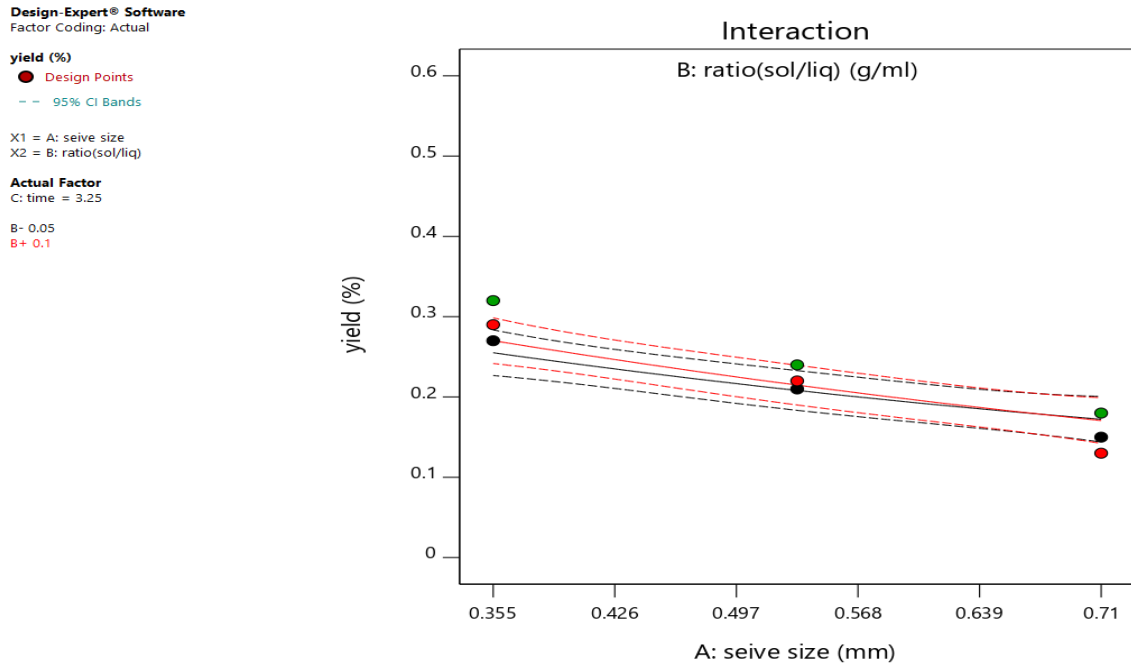


Figure 4.11: Effect of particle size and rumex abyssinicus to volume of ethanol ratio

Design-Expert® Software  
Factor Coding: Actual

yield (%)

● Design points above predicted value

○ Design points below predicted value

0 0.53

X1 = A: seive size  
X2 = B: ratio(sol/liq)

Actual Factor  
C: time = 3.25

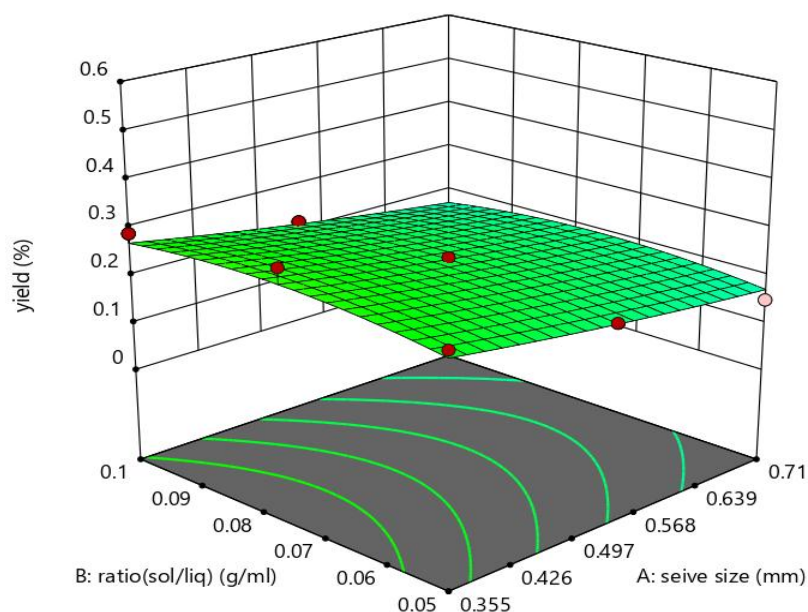


Figure 4.12: 3D and corresponding contour plot Rumex Abyssinicus and particle size

## 4.7 Experimental optimization of extraction conditions

There are three ways of optimization choices for Design-Expert software; numerical, graphical and point prediction optimization. In a numerical set of objectives for each response and depending on response designated different choices solution of optimization was given by expert design. One of the goals of the present study was to investigate the optimal process variables for an enhanced extraction yield of dye. The process variable such as particle size, extraction time, and rumex abyssinicus to volume of ethanol ratio was optimized. According to process variables for optimizing process variables the particle size, extraction of time, and rumex abyssinicus to volume of ethanol ratio were set of process variables used in the study. The process variable and optimal conditional was observed; extraction time of 3.25hr, particle size (0.5325mm), and rumex abyssinicus to volume of ethanol 0.075g/ml respectively and under the optimal condition, the value of yield of dye was 0.24%.

## 4.8 Characterization of dyes

### 4.8.1 Fourier transformation infrared (FT-IR) analysis dye

FTIR-spectra analysis was performed to determine information of functional group present on the dye and nature of bands. The range of standard broadband centered was identified in a table (4.7). The functional groups present in dye were determined by relating the vibration frequencies in wavenumbers of the sample spectrograph gained from an FT-IR spectrophotometer with those of an IR correlation chart. From figure (4.13) the FTIR spectroscopy of the extracted dye resulted in a range of phenol compound at the peak of  $3367.54\text{cm}^{-1}$ . This showed the presence of medium was in the region of  $(3200-3550\text{cm}^{-1})$  the functional group of Hydrogen bonded-OH stretching (alcohols and phenol). On the other hand, IR spectroscopy of the extracted dye resulted in the range of C-H stretching at a peak of  $2929.33\text{cm}^{-1}$ , this was shown C-H stretching occurred in the range of  $(2850-2950\text{cm}^{-1})$ . Additional FTIR spectroscopy of the extracted dye resulted in the range of C=O stretch at the peak of  $1731.92\text{cm}^{-1}$ , since the presence of medium was in the region of  $(1680-1780\text{cm}^{-1})$  was a functional group of C=O stretch (Ketones, Aldehyde, and Ester). IR spectroscopy of the extracted dye resulted in the range of amide stretching (C=O stretch) at a peak of  $1641.2\text{cm}^{-1}$ , this showed the range of  $(1690-1630\text{cm}^{-1})$  was shown that presence amide stretching (C=O stretch) functional group. IR spectroscopy of the extracted dye resulted in the range of H-C-H stretch and C=C aromatic group vibrational frequency at the peak of  $1376.39\text{cm}^{-1}$ . IR spectroscopy of the extracted dye resulted in the range of C-O-C and C-OH (Ethers, alcohols, and sugars) functional group at a peak of  $1215.88\text{cm}^{-1}$ , this indicated that the range of  $(1000-1300\text{cm}^{-1})$  was a functional group of C-O-C and C-OH (Ethers, alcohols, and sugars) occurred. FTIR spectroscopy of the extracted dye resulted in the range of C-O-C and C-OH (Ethers, alcohols, and sugars) functional group at a peak of  $1042.53\text{cm}^{-1}$ , this showed the presence of medium was in the range of  $(1000-1300\text{cm}^{-1})$  the functional group of C-O-C and C-OH (Ethers, alcohols, and sugars) occurred. IR spectroscopy of the extracted dye resulted in the range of =C-H bending vibration of alkenes and aromatic compounds at a peak of  $910.11\text{cm}^{-1}$ , this showed the presence of medium was in the range of  $(1000-650\text{cm}^{-1})$  was =C-H bending vibration of alkenes and aromatic compounds occurred. And IR spectroscopy of the extracted dye resulted in the range of bending

vibration of alkenes and aromatic compounds at a peak of  $864.36\text{cm}^{-1}$ , this was obtained in the range of  $(1000-650\text{cm}^{-1})$  bending vibration of alkenes and aromatic compounds occurred.

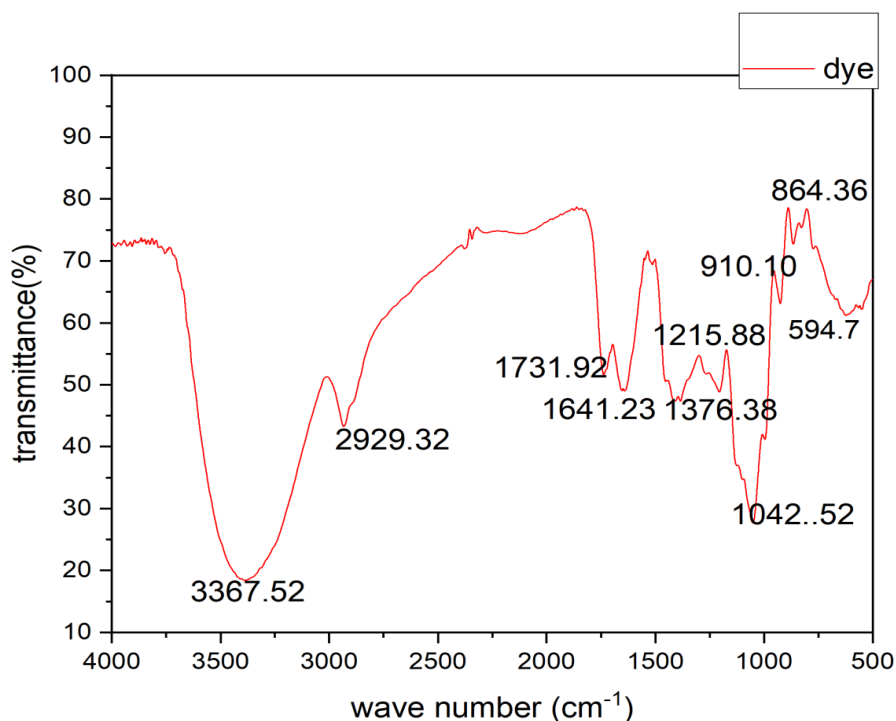


Figure 4.13: FTIR analysis of dye extracted from rumex abyssinicus

Table 4.7: Range of standard broadband centered for dye [4]

Functional group names	Characteristic wave number Absorption( $\text{cm}^{-1}$ )	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 compounds	1000-650	=C-H bending
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

#### 4.8.2 Characterization with UV-Visible Spectroscopy

The UV–Visible spectrum of the extracted natural dye was characterized by the major absorption maxima. A scan from 200 to 600nm was performed to generate the characteristic absorption spectra of the sample by filling of dye into the cuvette tube and placing it in the sample holder in a UV-Vis machine. The maximum wavelength that gave maximum absorption ( $\lambda_{\text{max}}$ ) was recorded at a wavelength of from spectrophotometer shown in figure (4.14). A maximum absorbance peak ( $\lambda_{\text{max}}$ ) was detected at 281nm with an absorbance of (0.908) using ethanol extraction. The characteristic spectra of the dye showed absorptions and the absorption appears at  $\lambda_{\text{max}} = 281\text{nm}$  (extracted from rumex abyssinicus) was observed which are due to the presence of more conjugated double bonds and the natural dye had strong absorbance in the UV-vis region. All the natural dyes from present are found to have poor absorbance in the visible region, they may not be suitable for solar cell purposes [69]. Extract natural dye from Eucalyptuscamaldulens leaf the absorption appears was at  $\lambda_{\text{max}} = 210\text{nm}$  which indicated the conjugate of the double bond [15].

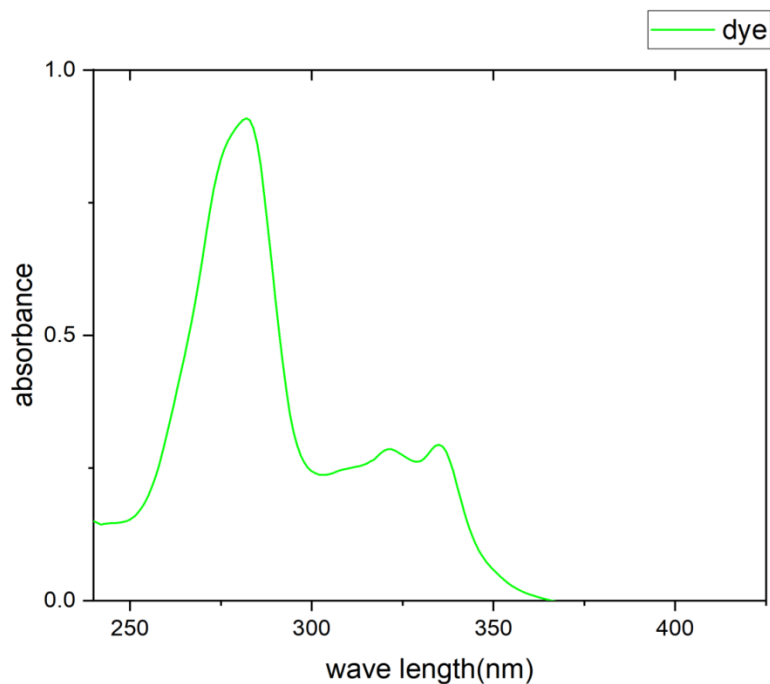


Figure 4.14: UV-Visible Spectroscopy dye

#### 4.9 Experimental design for Optimization of crayon

Table (4.8) below shows the result of the 24 experiment run was carried out according to response surface design. 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 others of the independent variables constant.

Table 4.8: summary of build information for design layout

File Version	11.1.2.0		
Study Type	Response Surface	Subtype	Randomized
Design Type	Box-Behnken	Runs	24
Design Model	Quadratic	Blocks	No Blocks

Build Time (ms)	99.00		
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Table (4.9) below showed the response of the absorbance of during design expert software was analyzed four variable and three-level design to study the simultaneous effect parameters on absorbance.

Table 4.9: Experimental design layout for absorbance of color

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	Run	A:Talc	B:Dye	C:Paraffin wax	D:Temprature	absorbance
		g	g	g	°C	
3	1	5	2	6	90	0.615
21	2	7	0.5	6	80	0.629
22	3	7	2	6	80	0.687
14	4	7	2	4	90	0.816
15	5	7	0.5	8	90	0.517
13	6	7	0.5	4	90	0.729
4	7	9	2	6	90	0.8
9	8	5	1.25	6	80	0.566
1	9	5	0.5	6	90	0.53
5	10	7	1.25	4	80	0.77
7	11	7	1.25	4	100	0.785
17	12	5	1.25	4	90	0.673
24	13	7	2	6	100	0.701
2	14	9	0.5	6	90	0.715
11	15	5	1.25	6	100	0.577
8	16	7	1.25	8	100	0.554
10	17	9	1.25	6	80	0.742
19	18	5	1.25	8	90	0.504
23	19	7	0.5	6	100	0.643
6	20	7	1.25	8	80	0.542

16	21	7	2	8	90	0.589
20	22	9	1.25	8	90	0.658
12	23	9	1.25	6	100	0.756
18	24	9	1.25	4	90	0.83

## 4.10 statistical model equation

### 4.10.1 Analysis of ANOVA for the quadratic model

The analysis of variance (ANOVA) was obtained from design expert software, which tells as the significance of different factors.

Table 4.10: Analysis of variance (ANOVA) for Response Surface of absorbance of color

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.2345	13	0.0180	61.33	< 0.0001	significant
A-Talc	0.0894	1	0.0894	304.11	< 0.0001	
B-Dye	0.0165	1	0.0165	56.11	< 0.0001	
C-Paraffin wax	0.1279	1	0.1279	434.96	< 0.0001	
D-Temperature	0.0005	1	0.0005	1.81	0.2078	
AB	0.0000	1	0.0000	0.0000	1.0000	
AC	2.250E-06	1	2.250E-06	0.0077	0.9320	
AD	2.250E-06	1	2.250E-06	0.0077	0.9320	
BC	0.0001	1	0.0001	0.1913	0.6712	
BD	0.0000	1	0.0000	0.0000	1.0000	
CD	2.250E-06	1	2.250E-06	0.0077	0.9320	
A <sup>2</sup>	0.0000	1	0.0000	0.0417	0.8424	
B <sup>2</sup>	0.0000	1	0.0000	0.0767	0.7874	
C <sup>2</sup>	0.0000	1	0.0000	0.0478	0.8313	
D <sup>2</sup>	0.0000	0				
Residual	0.0029	10	0.0003			

Lack of fit	0.0017	6	0.0002	0.08	0.6	not significant
Pure error	0.0018	7	0.00013			
Cor Total	0.2374	23				

The Model F-value of 61.5 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, C is 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

Design-expert was applied to analyze results on the extraction process and a second-order polynomial equation with the interaction terms was derived to express the absorbance of color and the final model equation in terms of a coded factor was presented by equations representing the variation of percentage of absorbance of color with independent factors.

Final Equation in Terms of Coded Factors:

$$\begin{aligned} \text{Color absorbance} = & +0.8330 + 0.0693A + 0.0278B - 0.0810C + 0.0053D + 0.0128AB - 0.0233AC \\ & + 0.0020AD - 0.0125BC + 0.0013BD - 0.0022CD + 0.0070A^2 \\ & + 0.0000B^2 + 0.0135C^2 + 0.0000D^2 \dots\dots\dots (4.3) \end{aligned}$$

The equation 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 of absorbance of color was affected by terms of talc (A), dye (B), paraffin wax (C), temperature (D), pure quadratic terms (A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup> and D<sup>2</sup>) and interaction quadratic terms (AD, AC, BD, and CD).

It was observed that absorbance of color increase with increase talc (A), dye(B), and temperature (D) which were a positive linear effect on the absorbance of color and decrease with paraffin wax (C). Pure quadratic term ( $A^2$ ,  $B^2$ ,  $C^2$  and  $D^2$ ) was a positive effect on the absorbance of the color of response. The interaction of interaction factor of talc and dye (AB), the interaction of factor of talc and temperature (AD) were positive linear effect on the absorbance of color and talc and paraffin wax (AC), interaction factor of dye and paraffin wax (BC) and paraffin wax and temperature (CD) were negative effects on the absorbance of color response.

Final Equation In terms of the Actual factor

$$\begin{aligned} \text{Color absorbance} = & +0.734944+0.025417\text{Talc}+0.012611\text{Dye}-0.019771\text{Paraffin wax}- \\ & +0.000300\text{Temprature}+0.0085000\text{Talc}*\text{Dye} -0.005812\text{Talc}*\text{Paraffin wax} \\ & +0.000100 \text{Talc}*\text{Temperature}-0.008333\text{Dye}*\text{Paraffin wax}+0.000167 \\ & \text{Dye}*\text{Temperature}-0.000112\text{Paraffin wax} *\text{Temperature}+0.001750\text{Talc}^2 \\ & +5.47171\text{E} - 16\text{Dye}^2 + 0.003375\text{Paraffin wax}^2 \\ & +0.000000 \text{Temperature}^2 \dots\dots\dots (4.4) \end{aligned}$$

Table (4.11) below showed the agreement between the predicted and adjusted value of model design was either fit statistics or not by considering the difference between them must less than 0.2.

Table 4.11: Fit Statistics between predicted and adjusted

Std. Dev.	0.0171	R <sup>2</sup>	0.9876
Mean	0.6637	Adjusted R <sup>2</sup>	0.9715
C.V. %	2.58	Predicted R <sup>2</sup>	0.9287
		Adeq Precision	28.9480

The Predicted R<sup>2</sup> of 0.9287 is in reasonable agreement with the Adjusted R<sup>2</sup> of 0.9715; i.e. the difference is less than 0.2.

Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 28.948 indicates an adequate signal. This model can be used to navigate the design space.

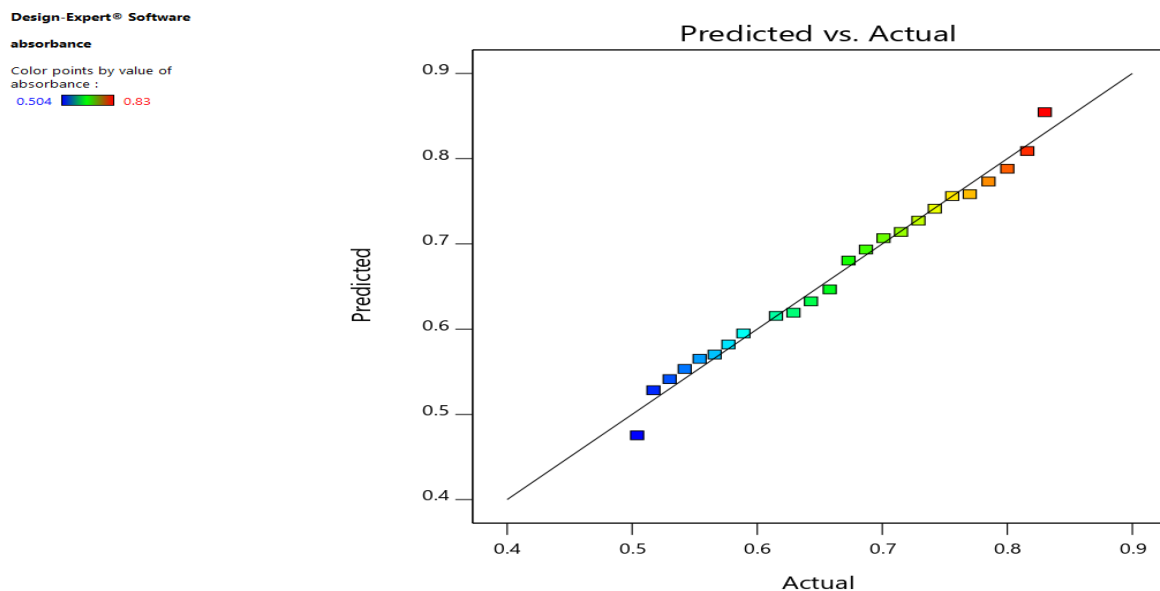


Figure 4.15: predicted versus actual value

## 4.11 Effect of process parameters on the absorbance of color

### 4.11.1 Effect of talc on the absorbance of color

The talc was one of the parameters involved in the percentage of absorbance of color that was crayon formulated from different ingredients by using the stirrer mixing method on a magnetic stirrer plate. There was a strong relationship between the mixing methods and the color of absorbance obtained from mixing ingredients.

From figure (4.16) the absorbance of color was correlated with the variable of talc, the absorbance of color was increased as the amount of talc was increased in the mixing. The amount of talc run from the lower level (5g to 9g) higher level at a fixed value of dye (1.25g), paraffin wax (6g), temperature 90 °C and as the absorbance of color using stirring mixing method was enhanced, amount talc was also increased, this means increasing the talc role in mixing to more contact between mixing and mixing was produce large amount absorption between mixing parameters and there was less caking of the product since talc is used for purpose of improving the feel of the product by preventing caking and by absorbing moisture

and help to cut down on friction and also during mixing the fine powder of talc was used for purpose of absorption of extracted dye with others ingredients.

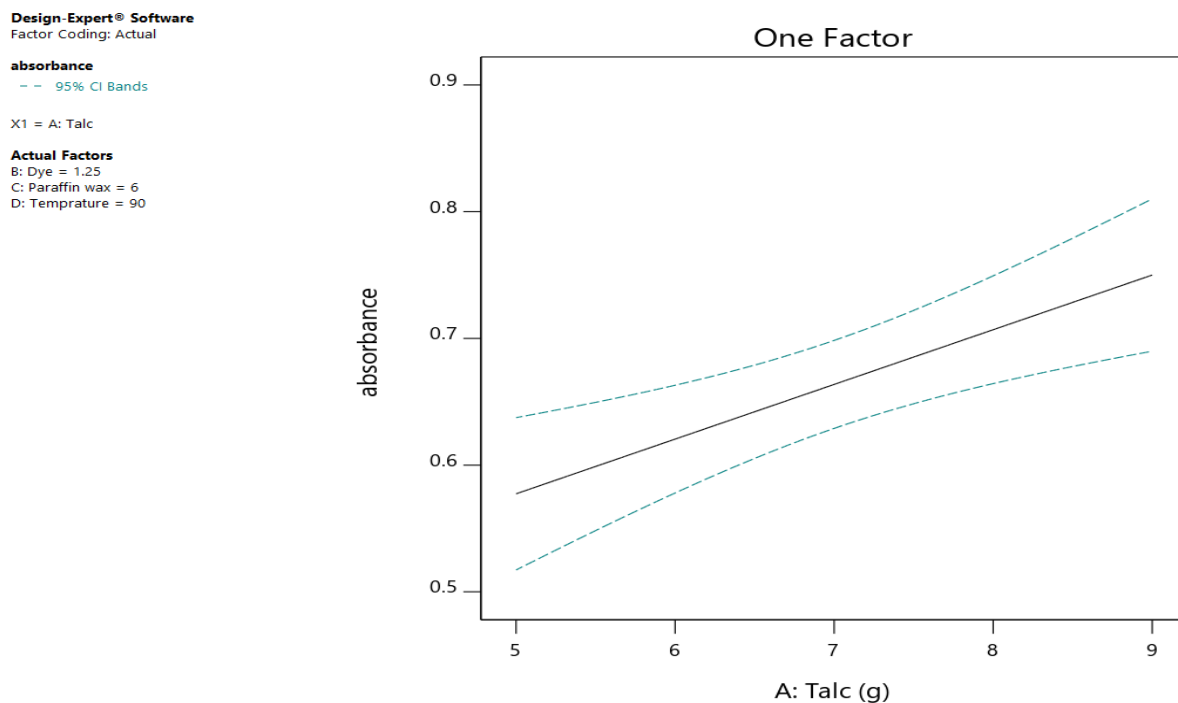


Figure 4.16: Effect of talc on the absorbance of color

#### 4.11.2 Effect of dye on the absorbance of color

The amount of dye was a key in the absorbance of color that was crayon formulated from different ingredients by using the stirring mixing method. There was a strong relationship between the mixing methods and the absorbance of color obtained from mixing ingredients deepened on the dye, due to the dye was used for coloring (that gave the colorant for crayon formulated from those each ingredient). From figure (4.18) the absorbance of color was correlated with the amount of dye, the absorbance of color increased as the amount of dye was an increase. The amount of dye runs from the lower level (0.5g to 1.25g) higher level as a fixed value of talc (7g), paraffin wax (6g), and temperature 90 °C. And. As the color absorbance using the stirring mixing method was enhanced, the amount of dye was also increased; this means increasing the dye during mixing was gives more colorant appear for purpose of drawing.

**absorbance**

-- 95% CI Bands

X1 = B: Dye

**Actual Factors**

A: Talc = 7

C: Paraffin wax = 6

D: Temperature = 90

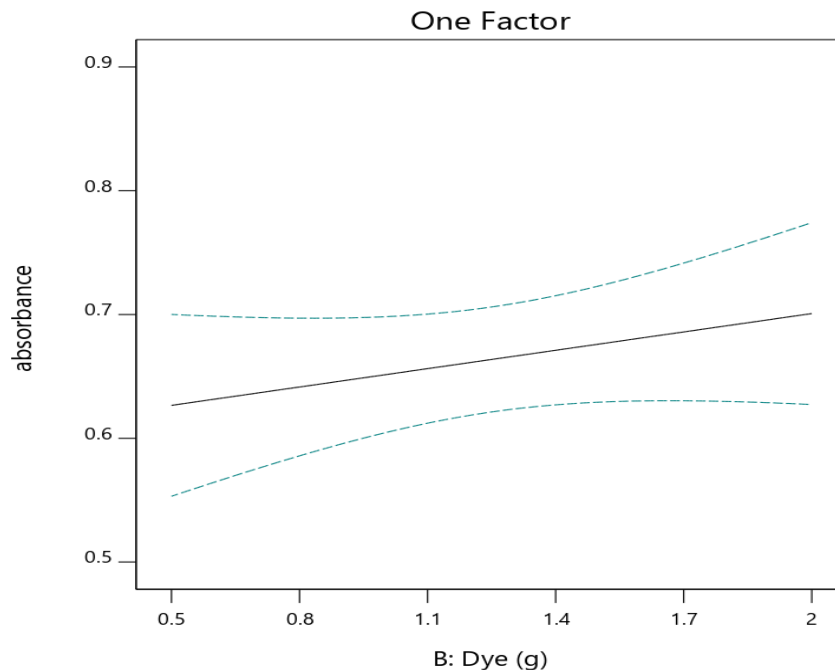


Figure 4.17: Effect of dye on the absorbance of color

#### 4.11.3 Effect of paraffin wax on the absorbance of color

From the graph (figure 4.18) the percentage absorbance of color was oppositely related with paraffin wax when a smaller size amount of paraffin wax gives high color absorbance while a larger amount of paraffin wax results in a lower absorbance of color. This shows as the intensity of color was increased when the paraffin wax was decreased and The amount of paraffin wax run from higher-level (8g to 4g) lower level at a fixed value of talc (7g), dye (1.25g), and temperature 90 °C, The reason is that paraffin wax was normally not mixed with dye extracted from the root of rumex, since paraffin wax unreactive in nature and lacking reactivity (affinity), but its mixed with dye when talc was used in the reaction, so if the amount of paraffin wax was increased the amount of color needed was reduced because the absorption of between mixing was low, but paraffin wax imparts satisfy strength and resistance breaking for the formulation of the product.

**absorbance**

-- 95% CI Bands

X1 = C: Paraffin wax

**Actual Factors**

A: Talc = 7

B: Dye = 1.25

D: Temperature = 90

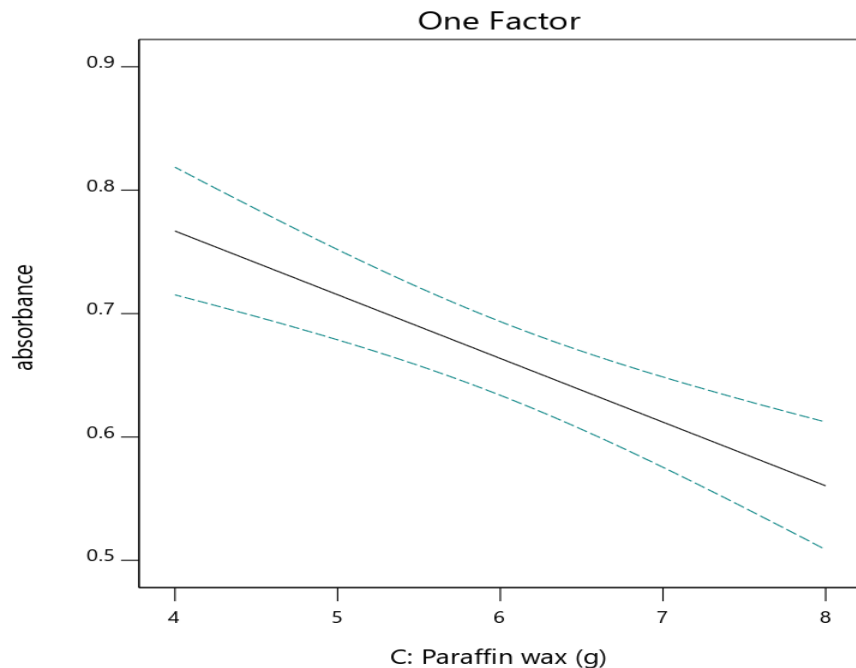


Figure 4.18: Effect of paraffin wax on the absorbance of color

#### 4.11.4 Effect of temperature on the absorbance of color

Figure (4.19) shows the absorbance of color was changed when the temperature was changed from 80°C to 100°C, at a fixed value of talc 7g, dye 1.25g, and paraffin wax 6g. According to the graph, color absorbance was partially not affected due to a change of temperature. The plot shows that the effect of temperature on the absorbance of color was small since the mixing ingredients at different temperatures were give the approach value of absorbance. The plate of temperature during mixing was used to give heating for purpose of mixing and the stirrings mixing of ingredient was from 2 to 3minutes (in a short period), so the effect of temperature in this short time on the mixing was low.

absorbance

-- 95% CI Bands

X1 = D: Temperature

Actual Factors

A: Talc = 7

B: Dye = 1.25

C: Paraffin wax = 6

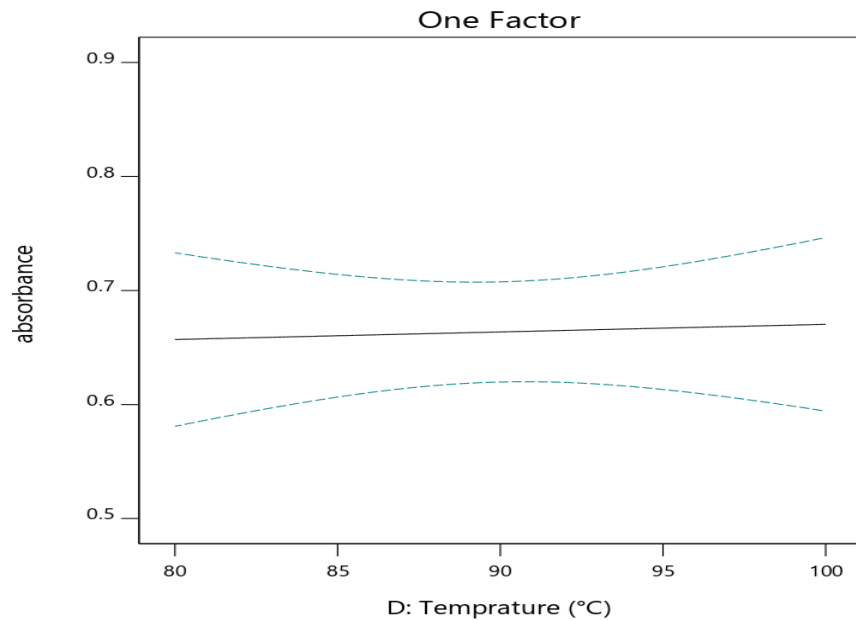


Figure 4.19: Effect of temperature on the absorbance of color

## 4.12 Effect of interaction parameters on the absorbance of color

The absorbance of color response as a result of two interactive variables while keeping the other variables constant was also investigated. Three dimensional (3D) response surface plots (plotted to recognize the interaction between the variables and the optimum level of each variable) and contours plots (presented the effect of two variables) were generated to regulate the optimum levels of the variables that were considered in this study. The plots were produced by keeping two variables fixed at the center point and changing the others within the experimental range. The resulting response surfaces displayed the effect of the amount of talc, paraffin wax, dye, and temperature on the absorbance of color. Therefore, in this case, four interaction factors were evaluated by the model equation.

AC- the interaction of Talc and paraffin wax

AB- the interaction of talc and dye

BD- dye and temperature

CD-paraffin wax and temperature

### 4.12.1 Effect of interaction of talc and paraffin wax on the absorbance of color

In figure (4.20) below shows that the Effect of the interaction of talc and paraffin wax on the color absorbance at a constant value of dye (1.25g) and temperature 90°C. When talc range from (5g to 9g) and paraffin wax from (4g to 8g), from this figure (4.21) it indicates that the maximum absorbance of color was achieved (0.83) at talc 9g and paraffin wax 4g. And the minimum absorbance of color was achieved (0.504) at talc 5g, and paraffin wax 8g. From this, it shows when paraffin wax was decreased and talc was increased, then the absorbance of color was increased, at talc 5g and paraffin wax 8g the absorbance of color was (0.505), at talc 9g and paraffin wax 8g absorbance of color was (0.658), at talc 5g and paraffin wax 4g absorbance of color was (0.67) and at talc 9g and paraffin wax 4g absorbance of color was (0.83). Figure (4.21) shows the response surface of 3D and counterplots developed in terms of the interaction of talc and paraffin wax. Talc was used for absorption of mixing and makes the product to give more color and paraffin used for the strength of the product, but it's not soluble with dye extracted because unreactive in nature, due to this amount of talc must increase to get more visibility of the color.

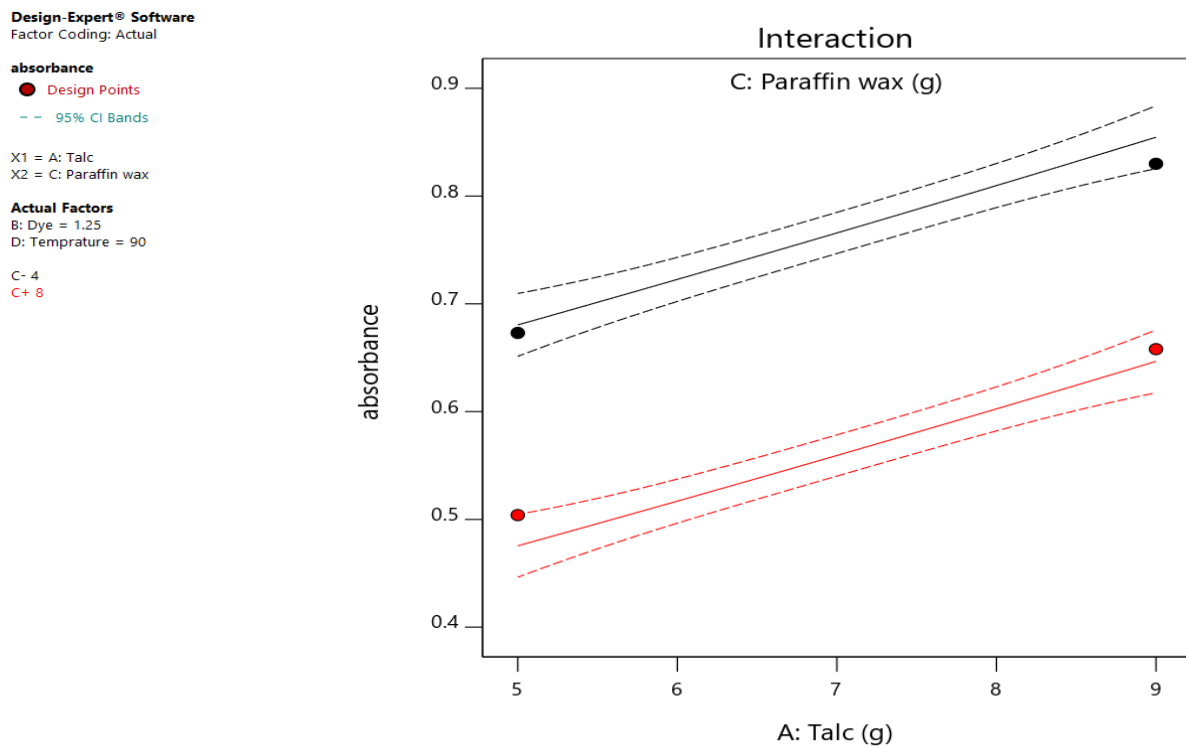


Figure 4.20: Effect of interaction of talc and paraffin wax on absorbance

Design-Expert® Software  
Factor Coding: Actual

**absorbance**

● Design points above predicted value

○ Design points below predicted value

0.504  0.83

X1 = A: Talc

X2 = C: Paraffin wax

**Actual Factors**

B: Dye = 1.25

D: Temperature = 90

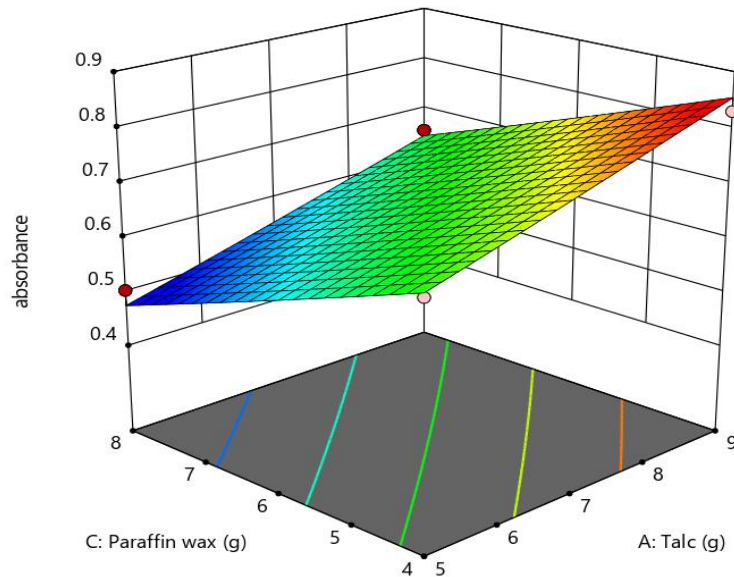


Figure 4.21: 3D and corresponding contour plot talc and paraffin wax

#### 4.12.2 Effect of interaction of talc and dye on the absorbance of color

the Effect of interaction of talc and dye on the color of absorbance at a constant value of paraffin wax 6g and temperature 90°C, when talc range from (5g to 9g )and dye from (0.5g to 2g). Figure (4.22) below indicated that the maximum absorbance of color was achieved (0.8) at talc 9g and dye at 2g. And the minimum absorbance of color was achieved (0.537%) at talc 5g and dye 0.5g. From this, it shows when the dye was increased and talc was also increased, then the absorbance of color was increased. At talc 5g and dye at 0.5 g, the absorbance was (0.53), at talc 5g and dye at 2g the absorbance was (0.615), at talc 9g, and dye at 0.5g the absorbance was (0.715) and at talc 9g and dye at 2g the absorbance was (0.8). Figure (4.23) shows the response surface of 3D and counterplots developed in terms of the interaction of talc and dye. Talc and dye are correlated during mixing because the dye was dissolved in the gradient in the case of talc and if the dye was more involved in the product the color of crayon and maximum amount of talc was involved in the mixing, the absorbance of color for purpose of the drawing was more visible.

Design-Expert® Software  
Factor Coding: Actual

absorbance

● Design Points  
-- 95% CI Bands

X1 = A: Talc  
X2 = B: Dye

Actual Factors  
C: Paraffin wax = 6  
D: Temperature = 90

B- 0.5  
B+ 2

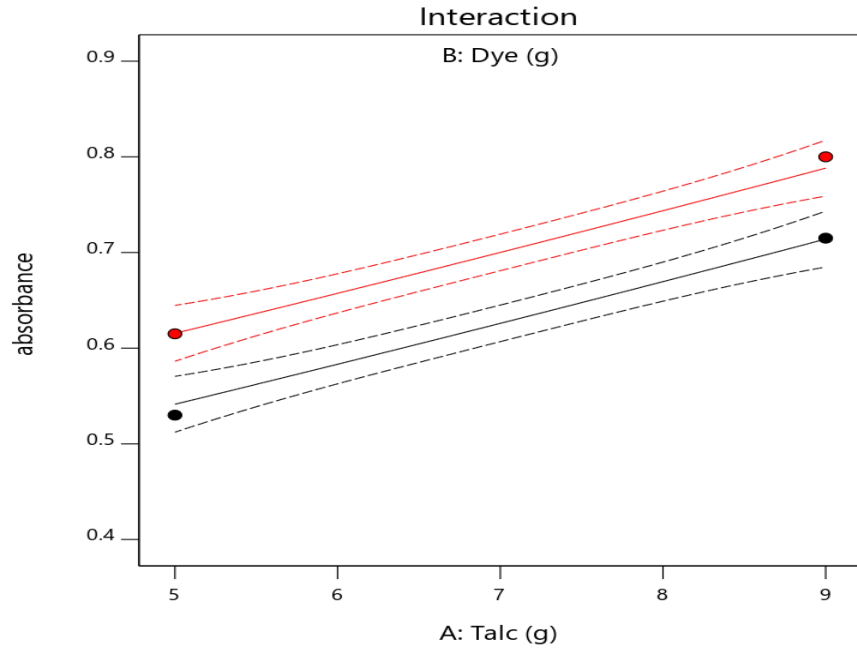


Figure 4.22: Effect of interaction of talc and dye absorbance of color

Design-Expert® Software  
Factor Coding: Actual

absorbance

● Design points above predicted value  
○ Design points below predicted value

0.504 0.83

X1 = A: Talc  
X2 = B: Dye

Actual Factors  
C: Paraffin wax = 6  
D: Temperature = 90

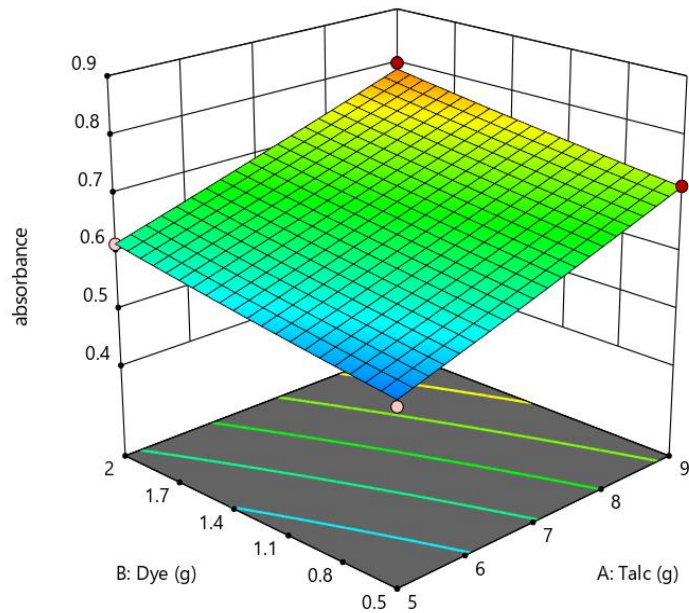


Figure 4.23: 3D and corresponding contour plot talc and dye

### 4.12.3 Effect of interaction of dye and temperature on the absorbance of color

The effect of interaction dye and temperature on the absorbance of color at a constant value of paraffin wax 6g and talc 7g, when dye range from 0.5g to 2g and temperature 80°C to 100°C. Figure (4.24) below indicated that the maximum absorbance of color was achieved (0.701) at temperature 100°C and dye at 2g. And the minimum absorbance of color was achieved 0.629 at 80°C temperature and dye 0.5g. From this, it shows when the dye was increased and the temperature was partially increased, then absorbance of color was increased (0.629), at temperature 100°C and dye 0.5g absorbance was (0.643), at temperature 80°C and dye 2g absorbance was (0.687) and at temperature 100°C and dye 2g absorbance was (0.701). Figure (4.25) shows the response surface of 3D and counterplots developed in terms of the interaction of temperature and dye. During the interaction of dye and temperature, the value of absorbance color was maximum at dye and temperature value also high, this indicates during mixing ingredient the dye which gives color for crayon was indicate good mixing occurred at a high temperature of the magnetic stirrer hot plate.

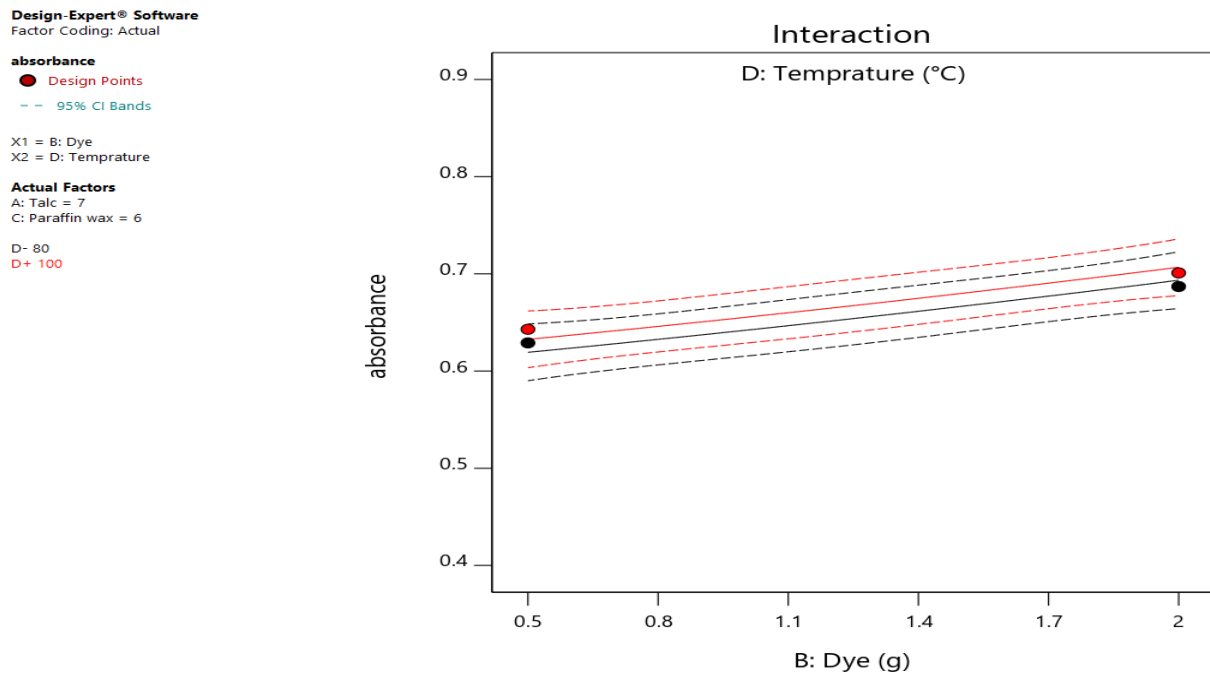


Figure 4.24: Effect of interaction of dye and dye on the absorbance of color

Design-Expert® Software  
Factor Coding: Actual

**absorbance**

● Design points above predicted value

○ Design points below predicted value

0.504  0.83

X1 = B: Dye

X2 = D: Temperature

**Actual Factors**

A: Talc = 7

C: Paraffin wax = 6

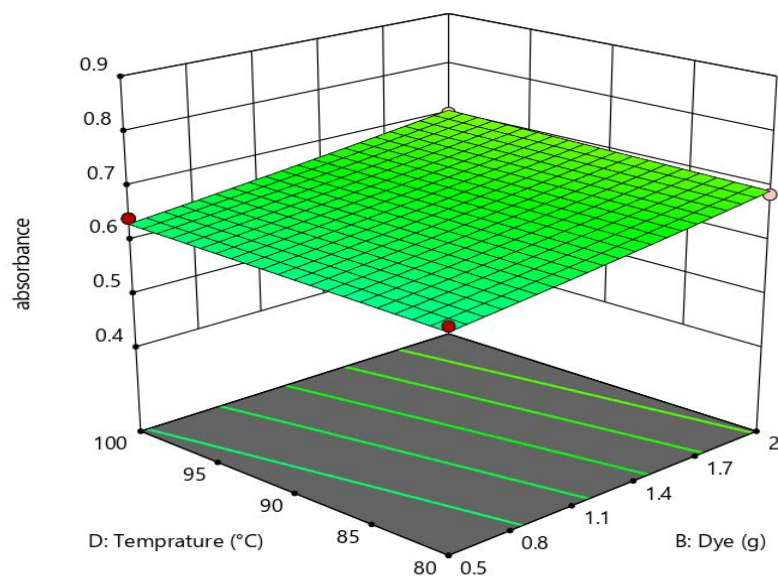


Figure 4.25: 3D and corresponding contour plot temperature and dye

#### 4.12.4 Effect of interaction of paraffin wax and temperature on the absorbance of color

From the figure below (4.26) the Effect of interaction paraffin wax and temperature on the absorbance of color at a constant value of talc 7g and dye 1.25g, when paraffin wax range from 4g to 8g and temperature 80°C to 100°C, it was indicated that the maximum absorbance of color was achieved (0.785) at temperature 100°C and paraffin wax at 4g. And the minimum absorbance of color was achieved (0.542) at 80°C temperature and paraffin wax 8g. From this, it shows when the temperature was increased and paraffin wax was decreased, the percentage of color absorbance was increased (0.542) at 80°C temperature and paraffin wax 8g, at 100°C temperature and paraffin wax 8g color of absorbance (0.544), at 80°C temperature and paraffin wax 4g color of absorbance (0.77) and temperature 100°C and paraffin wax at 4g color of absorbance (0.785). Figure (4.27) shows the response surface of 3D and counterplots developed in terms of the interaction of temperature and paraffin wax. During mixing time at high temperature, the paraffin wax was inflammable and cause the formulated crayon was losing its

strength and its effect on the hardness of crayon, so less amount of paraffin wax was recommended at high temperature during mixing.

Design-Expert® Software  
Factor Coding: Actual

**absorbance**

● Design Points  
-- 95% CI Bands

X1 = C: Paraffin wax  
X2 = D: Temperature

**Actual Factors**

A: Talc = 7  
B: Dye = 1,25

D- 80  
D+ 100

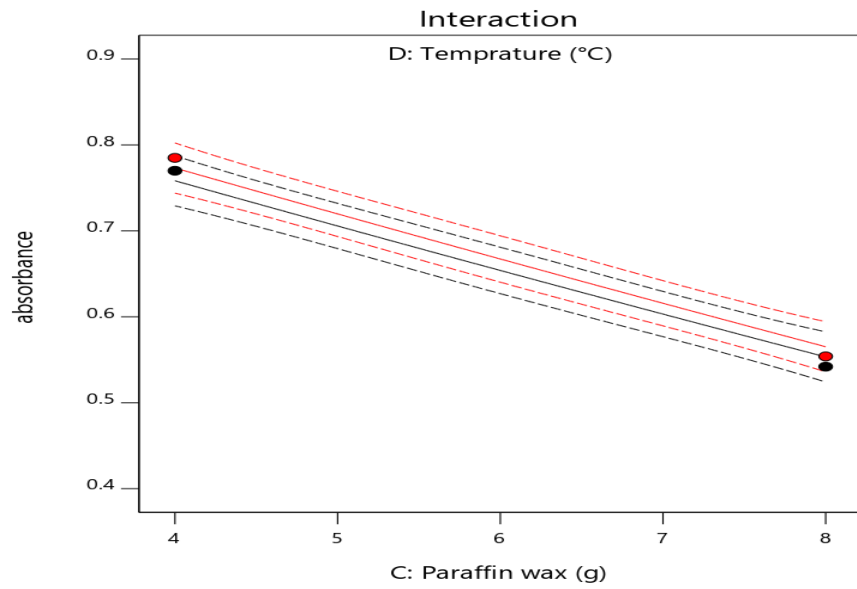


Figure 4.26: Effect of interaction of paraffin wax and temperature on the absorbance color

Design-Expert® Software  
Factor Coding: Actual

**absorbance**

● Design points above predicted value

○ Design points below predicted value

0.504  0.83

X1 = C: Paraffin wax

X2 = D: Temperature

**Actual Factors**

A: Talc = 7

B: Dye = 1.25

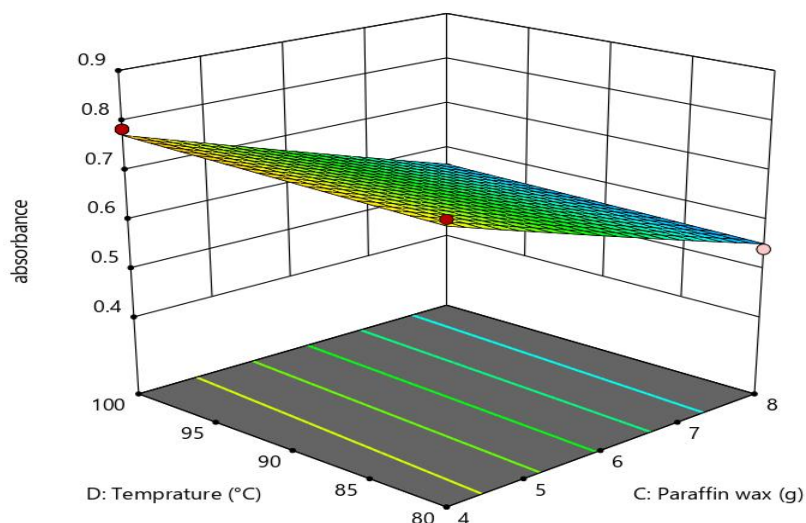


Figure 4.27: 3D and corresponding contour plot paraffin wax and temperature

### 4.13 Experimental compare of crayon formulation and commercial

The maximum percentage of color absorbance obtained was 0.830, at talc 9(g), paraffin wax 4(g), dye 1.25(g), and temperature 90°C respectively. Whereas the minimum percentage of absorbance of color absorbance obtained was (0.504), at talc 5(g), paraffin wax 9(g), dye 1.25(g), and temperature 90°C respectively. To comparing the color absorbance of formulated crayons and commercial crayons, the maximum percentage of color absorbance of the commercial (market) crayon was 0.68. This showed the formulated crayon has more absorbance than commercial crayon because the extracted dye used for colorant in formulated crayon has a high amount of absorbance than the colorant used for a commercial crayon. The absorbance was usually ranged from (0%) to (99%) and at (0%) there was no absorbance, but above zero percent there was the absorbance of value.



(a)



(b)

Figure 4.28: commercial crayon (a) and crayon formulated (b)

The figure above of (4.28) was indicating the picture of commercial crayon (a) and formulated crayon (b). Crayon formulated was molded by a manual machine (1cm diameter cm \*8.5cm height) that was a similar size to commercial crayon.

## 4.14 Characterization of crayon

### 4.14.1 Characterization of UV-Visible Spectroscopy

The absorption of radiation by a sample is measured at various wavelengths and plotted by a recorder to give the spectrum which is a plot of the wavelength of the entire region versus the absorption (A) of light at each wavelength, to calculate the bandgap of the samples. From figure (4.29), the UV–Visible spectrum of the optimum value of absorption was a draw. The formulated crayon was characterized by the major absorption maxima and compared with the commercial crayon that was similar color with formulated crayon.

A scan from 200 to 700nm was performed to generate the characteristic absorption spectra of crayon formulated and commercial crayon. The maximum wavelength that gave maximum absorption ( $\lambda_{\max}$ ) was recorded at a wavelength of from spectrophotometer shown in figure (4.31). A maximum absorbance peak ( $\lambda_{\max}$ ) of the formulated crayon was detected at 298.7nm with an absorbance of (0.8303) since it was formulated by using organic natural dye (extracted from rumex abyssinicus) color of the crayon was formed and good absorbance in the region of

UV because more conjugated double bond is formed in case of dye extracted from rumex. And a maximum absorbance peak ( $\lambda_{max}$ ) of the commercial crayon was detected at 305.5nm with an absorbance of 0.68, the moderate black color of commercial crayon good absorbance in the UV region. The electronic absorption spectra of various synthetic dyes in the wavelength range of 300 - 900nm and the maximum absorption of moderate black color were 310nm [69].

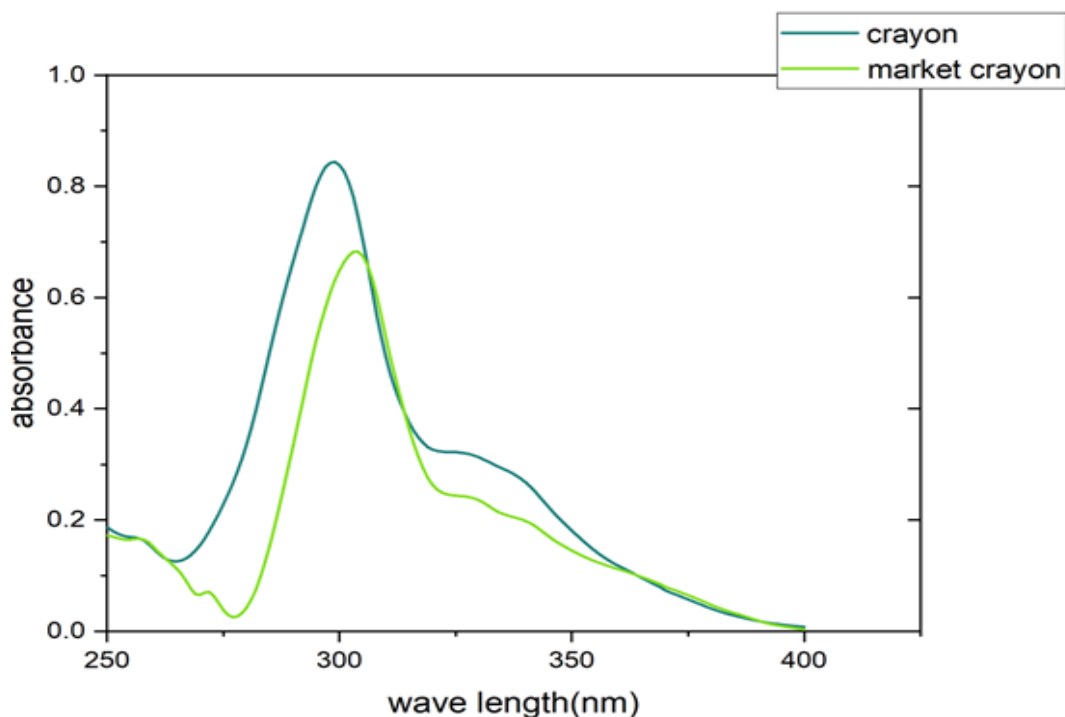


Figure 4.29: UV-Visible Spectroscopy for crayon formulated and commercial crayon

#### 4.14.2 Fourier transformation infrared (FT-IR) analysis of crayon

FTIR-spectra analysis was molecular spectroscopy which was used to characterizing organic and inorganic evidence. Characteristic IR Absorption Peaks of Functional Groups was dependent on a range of broadband centered [70].

From figure (4.30) analysis peak formed with a functional group, the peak of  $3697.91\text{cm}^{-1}$  attribute to the presence of N-H stretch vibration due to the range of wavenumber ( $3700\text{-}3500\text{cm}^{-1}$ ) was show the range of functional group N-H stretch vibration. The peak of  $3390.00\text{cm}^{-1}$  attribute to the presence of Hydrogen bonded -OH stretching (alcohols and phenol) due to the range of wavenumber of ( $3200\text{-}3550\text{cm}^{-1}$ ) was show the range functional

group Hydrogen bonded -OH stretching medium, this indicated: dye, talc, and stearic acid occurred at this peak of the -OH stretching structure. The peak of  $2939.79\text{cm}^{-1}$  attribute to the presence of C-H stretching of alkanes due to the range of wavenumber of ( $2990\text{-}2850\text{cm}^{-1}$ ) show the range was a functional group of C-H stretching of alkanes, it indicates paraffin wax occurred at a peak of  $2939.79\text{cm}^{-1}$ .

The peak of  $2849.90\text{cm}^{-1}$  attribute to the presence of C-H stretching of aldehyde due to the range of wavenumber of ( $2900\text{-}2800\text{cm}^{-1}$ ) was show the range of a functional group of C-H stretching of aldehyde. The peak of  $1627.42\text{cm}^{-1}$  attribute to the presence of C=C bending vibration of alkene due to the range of wavenumber of ( $1680\text{-}1620\text{cm}^{-1}$ ) was show the range functional group of C=C bending vibration of an alkene. And beeswax occurred at a peak of  $1627.42\text{cm}^{-1}$ . The peak of  $1497.65\text{cm}^{-1}$  attribute to the presence of C=C stretch aromatic compounds due to the range of wavenumber of ( $1625\text{-}1400\text{cm}^{-1}$ ) was show the range of a functional group of C=C stretch aromatic compounds, and also stearic acid occurred at a peak of  $1497.65\text{cm}^{-1}$ .

The peak of  $1002.44\text{cm}^{-1}$  attribute to the presence of C-F stretch alkyl due to the range of wavenumber of ( $1000\text{-}1400\text{cm}^{-1}$ ) was show the range of a functional group of C-F stretch alkyl. The peak of peak  $675.39\text{cm}^{-1}$  attribute to the presence of 2R -2H disubstituted, *cis* due to the range of wavenumber of ( $730\text{-}665\text{cm}^{-1}$ ) was show the range of a functional group of 2R -2H disubstituted, *cis*. from this dye occurred at this peak of  $675.39\text{cm}^{-1}$  ring structure. At a peak of  $490.64\text{cm}^{-1}$  C - I stretch alkyl stretching occurred since the range of C-I stretch alkyl was ( $< 600\text{cm}^{-1}$ ).

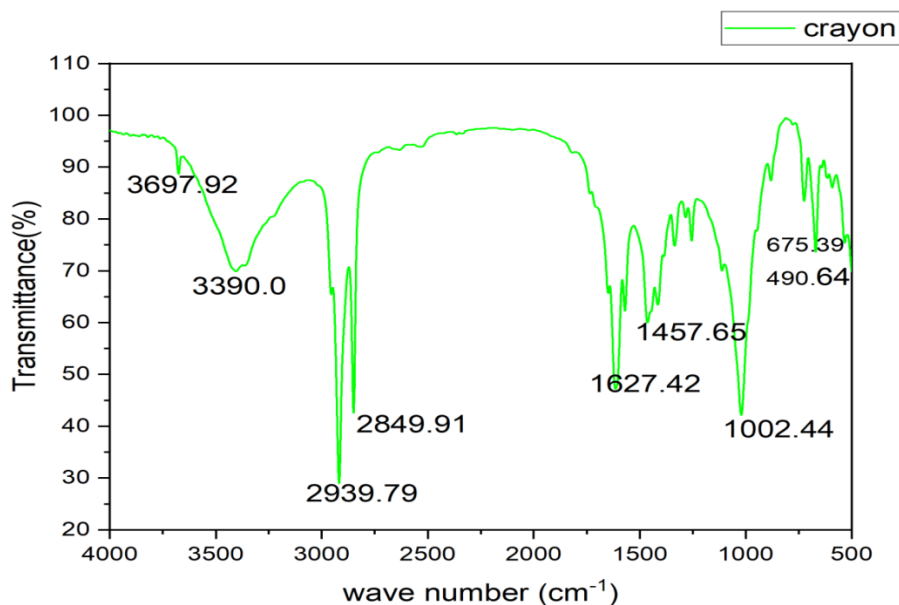


Figure 4.30: FTIR analysis of crayon

#### 4.14.3 Thermo Gravimetric analysis of crayon

TGA was used especially to regulate the decomposition of the crayon as the heating temperature changes. For crayon which shows either mass loss or gain due to decomposition, oxidation, or loss of volatiles and Thermogravimetric was also showed weight loss due to functional group decomposition of crayon and commercial crayon. The obtained TGA curves of formulated and commercial samples were shown in figure (4.31). According to the figure the TGA of these materials show three steps of mass loss, The first step there was a steady change of weight percentage of formulated and commercial crayon up to 112.01°C and also weight loss occurs close to 100°C was attributed to the moisture evaporation bonded on the surface and Elimination of some volatile compounds. The second step involved the crayon degradation, the Studies show that crayon formulated was degraded (maximum loss of weight) mainly between 207.72°C and 528.41°C, and commercial crayon was degraded (maximum loss of weight) mainly between 207.72°C and 660.81°C. From this, the commercial crayon was more difficult to decompose.

Due to the component occurred in crayon formulated and commercial crayon was major, not similar especially naturally dye extracted from rumex was used for formulated crayon rather than a commercial crayon. The third step involved the weight was linearly constant or steady

changed; this was showing its conversion to ash form. The weight was linearly constant for crayon start from 528.41°C and commercial start from 660.81°C.

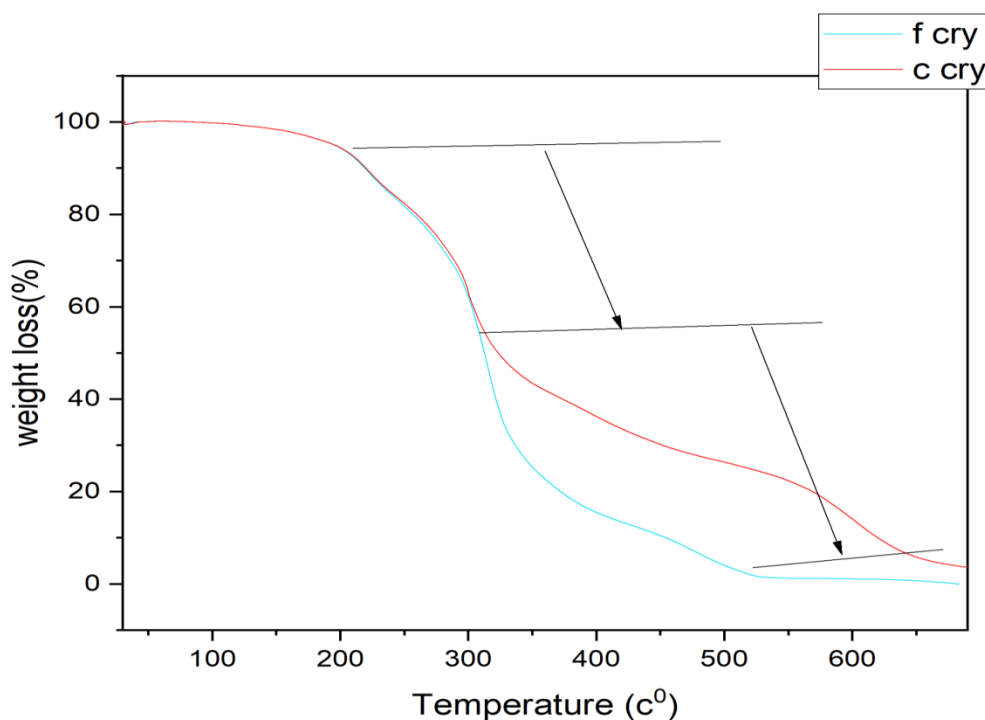


Figure 4.31: TGA for formulated crayon and commercial crayon.

In general, initially mass is more and temperature was low .when temperature goes to increase mass also comes down its respect to temperature because some molecules get either evaporator or degrade concerning thermo gravity. TGA was expressed in horizontal portion (steady) and downward portion. A horizontal portion was representing no loss in weight with an increase of temperature and the compound was thermally stable over the temperature range. A downward portion was indicating weight loss due to decomposition, dehydration, and formation of volatile produced at temperature.

#### 4.14.4 Tensile Strength test

In a tensile testing shaped sample of the crayon was placed in the grips of movable and stationary fixtures in a screwdriver device, which pulls the sample until it breaks and measures applied load versus elongation of the sample. Based on the tensile strength machine the input sample was dictated by the computer screen. According to this table (4.13) below, the tensile

strength and elongation at break of the formulated crayon compared with commercial crayon were shown.

Table 4.13: Stress-strain diagram for tensile test

Strain [%] F crayon	S [N/mm <sup>2</sup> ] F crayon	strain [%] C crayon	S [N/mm <sup>2</sup> ] C crayon
0	0	0	0
0.06	0.22	0.07	0.38
0.13	0.6	0.14	0.76
0.27	1.14	0.29	1.27
0.43	1.32	0.46	1.4
0.59	1.48	0.62	1.53
0.74	1.48	0.76	1.53
0.93	1.43	0.96	1.48
1.12	1.29	1.22	1.34
1.34	1.14	1.4	1.19

The force exerted at the time of breakage was the breaking strength [71] and the force exerted at maximum tensile before start to fracture was tensile strength. From figure (4.32) below it could be observed that the tensile strength value of formulated crayon was 1.48N/mm<sup>2</sup> and commercial crayon was 1.53N/mm<sup>2</sup> respectively. The commercial crayon showed better tensile strength than a formulated crayon, this could be attributed to the fact that it contains a less decomposed component and also less fracture. The results illustrate that there was a significant increase in tensile strength of formulated crayon from 0 N/mm<sup>2</sup> to 1.48N/mm<sup>2</sup> and filler loading was observed from 1.43N/mm<sup>2</sup> to 1.14N/mm<sup>2</sup>. And also for commercial crayon increase, tensile strength from 0 N/mm<sup>2</sup> to 1.48N/mm<sup>2</sup> and filler loading was observed from 1.48N/mm<sup>2</sup> to 1.19N/mm<sup>2</sup>.

The elongation at the break of the crayon provides an idea about the elastic behavior of the crayon. The crayon was first appearing in the elastic region and the point of tensile start to break was a plastic region that was the region of fracture of the component in the crayon. The

percentage of elongation of E (%) break strength of formulated crayon was 1.34% and for commercial 1.4%.

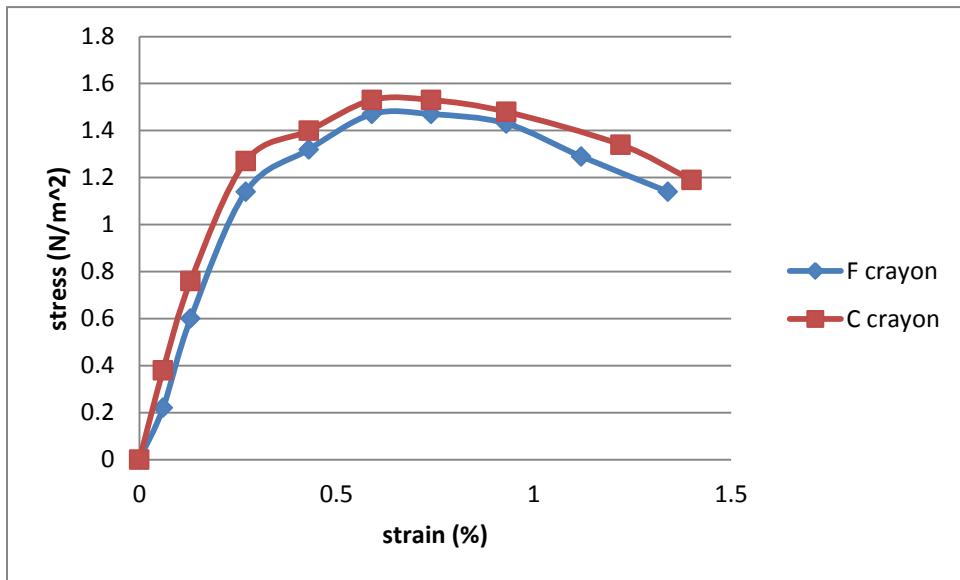
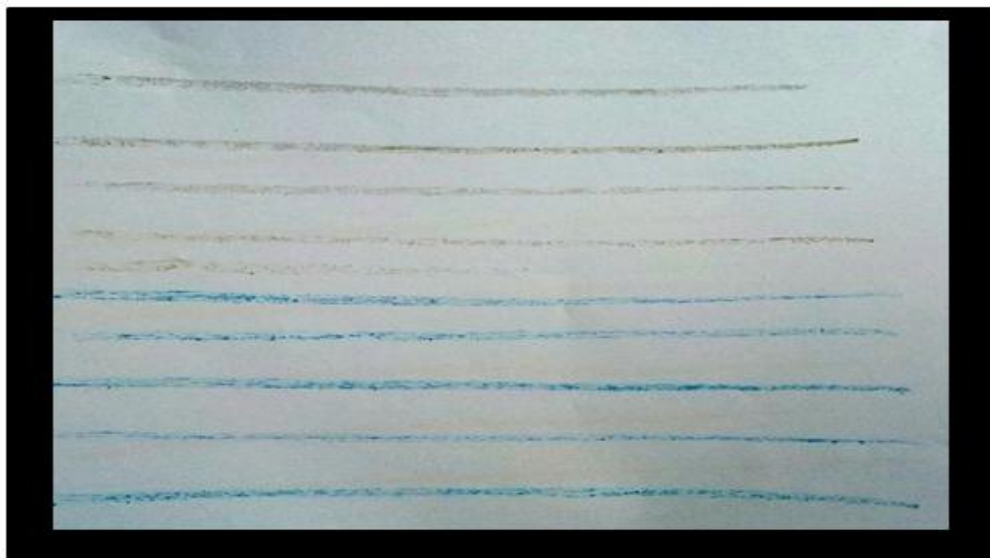


Figure 4.32: graph of stress versus elongation of break test

#### 4.14.5 Binding and durability of color

The formulated crayon color was binding on the material or not as compared to commercial crayon was initially dependent on the visibility of color on the material was binding on material or color was resisted. and from the figure below (4.33) the binding of commercial crayon and formulated crayon on the material paper was visible, they were binding on the material of paper and the durability of the formulated crayon was also defined according to sunlight involvement, its shows the paper was loss color or not. Therefore the material of paper did not lose the color of the crayon formulated that drowned on it. And it has similar color on the material when compared to the color of commercial crayon on the material. The durability of color that was colored the material and involved in sunlight, in-room and in the oven was not lost their color as the appeared on materials (appendix).and the formulated crayon used for color had similar color quality on the colored material when it's compared with commercial crayon.



(a)



(b)

Figure 4.33: Color of commercial crayon on paper (a) and formulated crayon (b)

## CHAPTER 5

### 5. Conclusions and Recommendations

#### 5.1 Conclusions

In this study, the root of rumex abyssinicus for dye synthesis and its application for crayon formulation was investigated. However, extraction was used for dye extraction and design expert software was analyzed three-variable and three-level design used to study the simultaneous effect of extraction time, rumex abyssinicus to volume of ethanol ratio, and particle size on the percentage of yield of dye. A statistically significant model ( $p < 0.0001$ ) was developed to describe the relationship between the yield of dye extracted and the chosen independent variables and the extraction conditions were optimized using response surface methodology and the statistical model showed a good fit with the experimental data ( $R^2 = 0.9891$ ). 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 time, particle size, and dried ground of rumex abyssinicus to volume of ethanol ratio) were significant and quadratic models were developed for predicting the responses.

Optimal values of extraction conditions that gave a maximum yield of dyes were selected from (27) alternative optimal solutions set by using numerical optimization of design expert. The maximum yield of dye was obtained after experimenting. As a result, it can be concluded that the yield of dye increases with an increase in rumex abyssinicus to ethanol ratio and extraction time, and decrease with particle size. FTIR was analyzed the functional groups of natural dyes and the double beam UV-vis spectrophotometer investigated the maximum wavelength that gave the highest absorbance of the color.

Design of an experiment for RSM box Behnken of a four-variable, three-level was studied the simultaneous effect of extraction talc, dye, paraffin wax, and temperature of magnetic stirrer on the response of maximum absorbance of color. A statistically significant model ( $p < 0.0001$ ) was developed to describe the relationship between the absorbance and the chosen independent variables and The statistical model showed a good fit with the experimental data ( $R^2 = 0.9876$ ). ANOVA showed that the effects of all variables (paraffin wax, talc, dye, and temperature) were significant and quadratic models were developed for predicting the responses. And the effect of

parameters (paraffin wax, talc, dye, and temperature) on the absorbance of color was studied and As a result, it can be concluded that absorbance of color increased with increase talc, dye, and temperature of magnetic stirrer and decrease with paraffin wax. UV-vis was shown a maximum absorbance of the color formulated crayon higher than a commercial crayon. FTIR was shown characteristic IR Peaks of Functional Groups in crayon formulated and TGA was used especially to regulate the decomposition of the crayon as the heating temperature changes and it indicates the temperature degradation of the commercial crayon was more difficult than a formulated crayon. Tensile strength test developed the braking strength of crayon formulate by comparing with commercial crayon and the commercial crayon was more strength than a formulated crayon. The formulated crayon color was also binding on the material and as compared with commercial crayon.

## 5.2 Recommendations

Based on the present study finding, the following recommendations are forwarded

- ❖ Storage techniques of *rumex abyssinicus* could be studied for the extraction of natural dye
- ❖ Further research work is needed on comparison of yield of natural dye *rumex abyssinicus* by different extraction technology such as steam distillation, supercritical fluid extraction, and aqua extraction with soxhlet extraction method
- ❖ Further research work on the remaining varieties of Ethiopian *rumex abyssinicus*
- ❖ The country should invite and encourage investors who are interested to work on value-added products like the production of crayons from organic natural dye locally instead of importing the crayon from abroad. This may create job opportunities for the employees and save valuable foreign exchange
- ❖ Economic analysis needs to be investigated to compare the cost of a formulated crayon with commercial crayon
- ❖ Additional studies are needed to formulate the different color of crayon by using other mordants

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## APPENDICES

### Appendix A: proximate analysis of rumex abyssinicus and extraction of dye



Collected rumex



washing root Rumex



milling sample by knife



Oven-dried rumex



sieve analysis



soxhlet extraction method



Rotary evaporator



dye

**Appendix B:** photos of crayon formulation



Paraffin waxes melt



beeswax melt



Dye



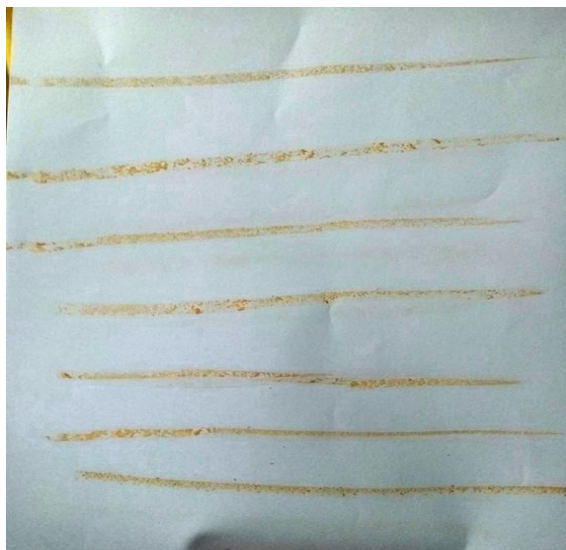
stearic acid



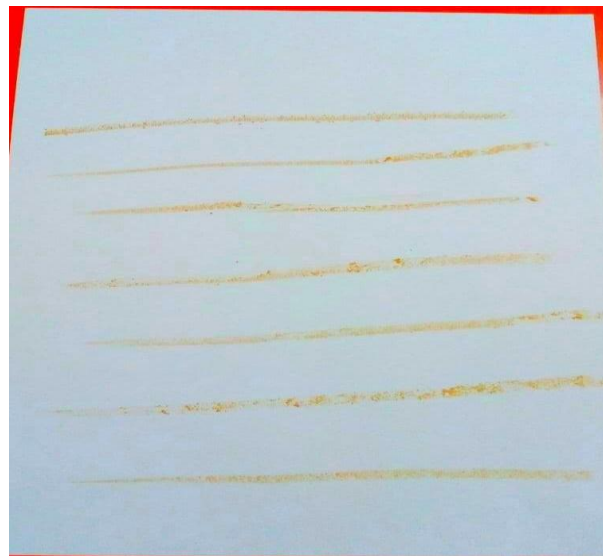
Talc



crayon



Durability for 7days (sunlight)



Durability for 7days (in the room)



Durability for 2days (an oven)

**Appendix C:** Laboratory equipment's



Sieve analysis



Ball mill



UV-vis spectroscopy



Digital camera



Tensile strength test



Magnetic stirrer