

**EXTRACTION, CHARACTERIZATION AND APPLICATION OF NATURAL DYE
FROM *Nesorgodonia papaverifera* AND *Berlinia grandiflora***

BY

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JULY, 2017.

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BY

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partial Fulfilment of the Requirement for the award of Master of Science (M.Sc) in
Organic Chemistry**

JULY, 2017.

DECLARATION

I hereby declare that this work titled “Extraction, Characterization and Application of Natural Dye from *Nesorgodonia papaverifera* and *Berlinia grandiflora*” is my original work and has not been previously submitted to this or any other University for the purpose of the award of any degree. All citation and sources of information are clearly acknowledged by means of reference.

ONYESOM IFEANYICHUKWU EMMANUEL

CERTIFICATION

I certify that this research work titled “Extraction, Characterization and Application of Natural Dye from *Nesorgodonia papaverifera* and *Berlinia grandiflora*” was carried out by Onyesom Ifeanyichukwu Emmanuel in the Department of Chemistry, Delta State University, Abraka.

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Date

DR. J. O. Otutu
(Head of Department)

Date

DEDICATION

This work is dedicated to Almighty God, the Father of Grace for His love and His guidance throughout this work.

It is also dedicated to my lovely wife Mrs. Esther Onyesom and to my daughter Miss Emmanuella Chiamaka Onyesom for their ceaseless prayers and supports throughout the course of this work.

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ABSTRACT

Natural dyes were extracted from the stem bark of *Nesorgodonia papaverifera* and *Berlinia grandiflora* using methanol, water, acetone, methanol KOH and acetone KOH as solvents at different temperatures and time. Of all the solvents used, water extracted most for *Berlinia grandiflora* while acetone was found to be the best solvent for the extraction of colourants from *Nesorgodonia papaverifera*. The mixture of each dye extract was separated using Column Chromatography and the purity was monitored using Thin Layer Chromatography (TLC). The purified dye extracts were characterized using GC/MS, IR, UV-Visible, ^{13}C NMR and ^1H NMR analyses. The results of the characterization suggested the presence of OH, CH_3 , CH_2 , CH, $\text{C}\equiv\text{C}$, $-\text{C}=\text{C}-$, OCH_3 , C-C, C-O-R, C=O functional groups in the dye extracts. The chromophores present in the dye extract are C=O and $-(\text{C}=\text{C})_5$ – for *Nesorgodonia papaverifera* and $=\text{C}-\text{C}=\text{C}-\text{C}=\text{O}$ and $-\text{C}=\text{C}-$ for *Berlinia grandiflora*. The natural dye extracts were used in the dyeing of nylon and cotton fabrics without a mordant and also with stannous chloride and potassium dichromate mordants. The wash fastness, light fastness, rubbing fastness and percentage exhaustion were evaluated. The results show that all the fastness properties of the dye extracts on the fabrics were improved on application of mordants.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

The use of synthetic dyes in textile industries has really posed a great threat to health and people are therefore vigilant of these environmental effects. This has led to the substitution of the synthetic dyes with the natural ones especially the ones extracted from plants in textile industries (Deo and Desai, 1999). Natural dyes are biodegradable, non-toxic and align well with the natural ecosystem compared to the synthetic ones (Maria *et al.*, 2010). Therefore, different species of plants, minerals and animal origins which centres attention on the revival of waste and eco – friendly materials were identified and applied on different fabrics in textile industry (Colchester, 2007).

The increase in the demand for natural dye instead of their counterpart (synthetic) is as a result of their low toxicity. Synthetic dyes are dangerous, life threatening and carcinogenic. It takes a very long time to break down when released to the natural ecosystem (Versimo *et al.*, 1991). To reduce the side effects of the hazard caused by synthetic dyes in the course of their production, this could be is therefore substituted by natural dyes. Natural dyes are eco-friendly and non-toxic colourants specifically for health sensitive applications such as food colouration and dyeing of infant textile and leather garments. Due to intensive and vast use of synthetic dyes, the use of natural dye has decreased greatly in textile industries. But still, in the last ten years, the application of natural dyes has increased in the world due to high demand by various industries as a result of the new environmental law established by different countries.

Natural dye can provide a wide range of aesthetic shades with a high grade of colour fastness (Ekrami *et al.*, 2011). Hence there are many research works going on presently across the globe on the application of plant dye in textile industry and the regeneration of natural dyes as alternative to synthetic dyes (Acguah and Oduro, 2012).

In Africa continent, plants has been extensively used for the extraction of natural products for drugs, pesticides and herbicides (Mayunga, 2007). Notwithstanding, light effort have been put in place in Africa in search of natural dyes compounds for textile industries. Africa as a continent is

blessed with several plant species with high capacity to produce natural products with colorants which could be used as dyes for textile coloration. But most of these plants were not exploited for such purpose, unknown phytochemically and undocumented. Hence, a large reservoir of new dye molecules awaits discovery.

In this research work, extraction of natural dyes from *Nesorgodonia papaverifera* and *Berlinia grandiflora* was selected for exploitation. Dyeing of cotton and nylon fabrics with the extracted dyes and spectral characterization of the dyed fabrics are reported.

1.2 Aim of the Study

The aim of the study is to extract, characterize and apply natural dyes from *Nesorgodonia papaverifera* and *Berlinia grandiflora* on cotton and nylon fabrics.

1.3 Objectives of the Study

The objectives of the study are to:

- i. extract natural dyes from *Berlinia grandiflora* and *Nesorgodonia papaverifera* using different solvents.
- ii. apply natural dyes on both synthetic and natural fibers (nylon and cotton)
- iii. determine the fastness properties of the dyes on cotton and nylon fabrics.
- iv. determine the percentage of exhaustion on fabrics.
- v. Characterize the dyes using U.V visible spectrophotometer, I.R spectrophotometer, Gas Chromatography - mass spectrophotometer (GCMS) and NMR spectrophotometer.

1.4 Scope of the Study

There are thousands of plants and animals which contains colourants that can be used as natural dyes. This present study is therefore focused on the extraction of natural dyes from two major tree bark namely;

1. *Nesorgodonia papaverifera*
2. *Berlinia grandiflora*.

1.5 Justifications

Recently there has been growing interest in using natural colourant for dyeing various materials because these dyes are believed to be more economically friendly, exhibit better biodegradability and are more environmentally friendly than synthetic dyes. Also most natural dyes are only applied to natural fibers. So this study will profer solution to the activities and the uses of natural dyes on synthetic fibers such as nylon. It will therefore be appropriately to undergo this study to improve information on this dyes of natural products and this will enhance the proper usage of them. This study will also create employment opportunities for Nigerians. It will also reduce exploitation of people most times because the major source of colourants presently is the imported synthetic dyes.

CHAPTER TWO

LITERATURE REVIEW

Before 19th century, natural dyes extracted from plants were the only dyes being used to colour textiles. There was nothing like inorganic pigments and dyes from animal origin.

Due to the introduction of less costly and cheaper synthetic dyes natural dyes started going into extinction as it is being substituted with cheaper synthetic dyes. This continued until cultivation of dye plants ceased due to complete substitution. In recent times, the use of some synthetic dyes has band in some European countries due to their toxicity. People started to be more sensitive to the effects brought about by the synthetic dyes (Deo and Desai, 1999). This has led to the resurgence of natural dyes (Maria, *et al.*, 2010).

2.1 Dyes

A dye can be generally defined as a coloured substance that has affinity to the substance to which when applied to a substrate, impacts colour to the material (Verissimo *et al.*, 1991). Natural dyes are generally applied in aqueous solution and they require a mordant to improve the fastness properties on the dyed fabrics. Dyes and pigments absorb and reflects light at certain wavelength to give human eye the sense of colour because they both absorb wavelengths of light more than others. The basic difference between a dye and a pigment is that pigments are generally insoluble and have no affinity for the substrate.

The wavelength of light absorbed is also affected by constituents on the electron-withdrawing ability or election donating groups and also through the position they occur. Notwithstanding, the colour observed for a given coloured substance is the reflected complementary colour of the substance having absorbed a particular wavelength within the visible spectrum. The table below shows the parts of complementary colours and wavelengths absorbed (Graham, 1972).

Table 1.1: Absorbed and Reflected Colours

| Wavelength (λ) | Colour – absorbed | Complementary |
|--------------------------|-------------------|---------------|
| 400 – 435 | Violet | Yellow- green |
| 436 – 480 | Blue | Yellow |
| 481 – 490 | Greenish- blue | Orange |
| 490 – 500 | Bluish – green | Red |
| 501 – 560 | Green | Purple |
| 561 – 580 | Yellow – green | Violet |
| 581 – 595 | Yellow | Blue |
| 596 – 605 | Orange | Green |
| 606 – 750 | Red | Blue – green |

If a substance absorbs all visible light with the exception of one band which it reflects, the substance will have the colour of that reflected band. Therefore a substrate will appear purple because it absorbs the green portion of the spectrum visible spectrum except purple. The shades however will be different. Apparently no dye gives a pure shade, that is does not reflect only one band of wavelength.

2.2 Classification of Dyes

The two major types of dyes are the natural dyes and synthetic or man-made dyes. The major source of natural dyes are plants, animal and some basic minerals. The synthetic dyes are man-made organic dyes which are made in the laboratory. Different types of chemicals are synthesized for the production of synthetic dyes. Some of the synthetic dyes also contains metals.

2.2.1 Synthetic Dyes

The first man-made or synthetic organic dyes called Mauveine was discovered by William Henry Parkin (1856). Several thousands of dyes have since been prepared in the laboratory and because of generally improved properties imparted upon the dyed materials, it therefore replaced the traditional natural dyes (Agarwal, 2008).

A dye whether natural or synthetic is used not only to just colour the surface of fibers but it must fix with the fiber and becomes part of it so that after dyeing, the fiber will not be affected during

the process of washing, dry cleaning etc with organic solvent. The dye should be able also to give fastness to heat, bleaching and light (Eforia, 2010)

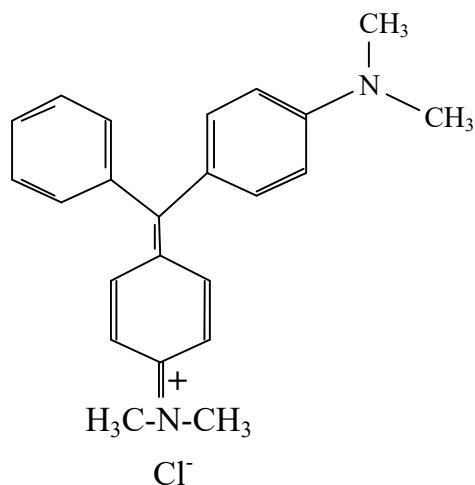
The global consumption of textile is estimated at around 30million tonnes, which is expected to grow at the rate of 3% per annum. Therefore such a huge amount of required textile materials cannot be dyed with natural dye alone. Hence, the used of eco-safe synthetic dyes is also essential (Samanta and Agarwal 2009).

Synthetic dyes used in the textile industry are briefly described below:

Basic Dyes

These type of dyes are also referred to as cationic dyes and are salts of organic colour bases. They are characterized by the presence of a basic ammonium group. It may also be present as a part of a heterocyclic ring as a tetravalent atom.

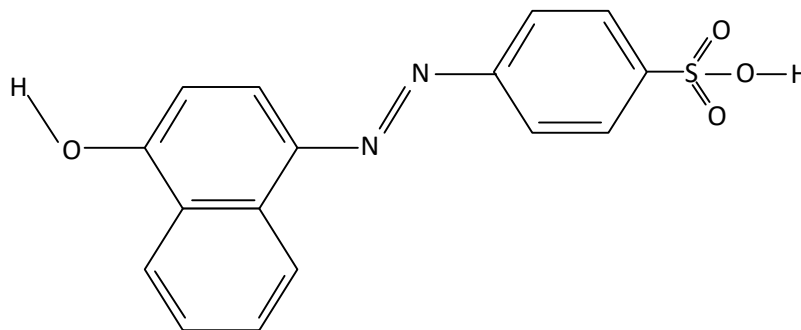
Basic dyes posses cationic functional group such as $-NR_3^+$ or $=NR_2^+$. The name basic dyes refers to when these dye were still used to dye wool in alkaline bath. Basic dyes performs poorly on natural fibre but does well in acrylics. An example of basic dye is shown below.



In the this case the charge is delocalized across the molecule but in some basic dyes, it is located on a single nitrogen atom

Acid Dyes

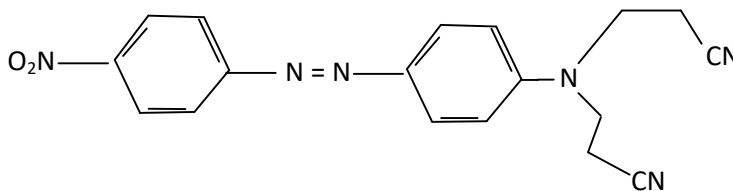
Acid dyes are highly soluble in water and have very good light fastness compared to basic dyes. They contain acid groups usually sulphonic groups which are present as sodium sulphate salts. This group makes it to be highly soluble in water thereby giving the dye molecule a negative charge. Hence, acid dyes are generally anionic. Though in an acidic solution, the $-NH_2$ functional group of the fibres are protonated to give a positive charge $-NH_3^+$. This charge reacts with the negative dye charge to form ionic interactions. Acid dyes can be subdivided into two. These are acid levelling dyes and acid-milling dyes. An example of acid dye is Alizarine (Mason, 2014).



Disperse Dyes

Disperse dyes are sparingly soluble in water and they can react with polyester chains to form dispersed particles. They are mostly used to dye polyesters and are also used in minute form dyeing cellulose acetates and polyamides. The accepted structure of disperse dye is small planar and non-ionic with attached polar functional groups like $-NO_2$ and $-CN$. The dye is usually applied under pressure at a high temperature of about 129°C . At this temperature, thermal agitation causes the polymer structure to become loose and less crystalline opening gaps for the dye molecules to enter. The interactions between, the dye molecules and polymer is Van der Waal force.(Dora, 2013).

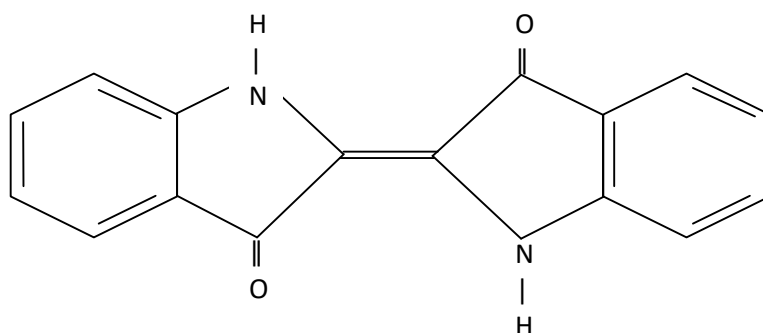
The most important class of disperse dyes is the azo class. Below is a structure of an azo dye



Vat Dyes

Vat dyes are common examples of the cross over between dyes and pigments. It is planar and contains numerous rings. These numerous rings helps to strengthen the attractive Van der Waal forces between the dye and the fibres.

Vat dyes does not dissolve in water but may be made soluble through alkali reduction using sodium dithionite (a reducing agent) in the presence of sodium hydroxide. (Mason, 2014). Below is an example of a vat dye.



2.2.2 Natural Dyes

Natural dyes are those colourants that are obtained from animals and plants. They are dyes produced by some plants and animals living in nature without any chemical transformation. Root , stem, leaf and flowers of the plants are used fresh and dried. For insects containing dyestuff the female species are dried and used after grinding (Mussak and Bechtold, 2009).

History of Natural Dyes

Colour is one of the elements of nature that made human living more aesthetic and fascinating in the world .They are supposed to be associated with emotions, human quality, seasons, festival and passion in our life. In the past at the dawn of civilization, the people tried to ornament their surrounding similar to that of natural colour observed in plant soil, sky and other source. This gave birth to a new science of colour from natural origin (Schetky *et al.*, 1986).

The art of dyeing is as old as human civilization. From the historical record, it is learnt that natural colourants were available to people during Greco-Roman period. The use of materials coloured or dyed with natural colourants is evident with the wall paintings of Ajanta Ellora and Sithannvasal and they still demonstrate the efficacy of dyeing craft that had been inherited from ancient time in India. (Grierson, 1980). Ancient Egypt hieroglyphs contain a thorough description of the extraction of natural dye and their applications in dyeing. Further developments extending over many thousands of years led to rather complicated dyeing process and high quality dyeing (Grierson, 1989).

2.2.2.1. Sources of Natural Dyes

Natural dyes fall into three categories based on their origin or sources. These are;

- i. Plant/ vegetable origin
- ii. Insect/ animal origin
- iii. Mineral origin

Plant Origin

Colourants derived from leaves, barks, trunks, fruits and flowers of plants fall under this category. In Nigeria over 800 plant species have been identified as useful sources of dyes. Some examples of dye sources are mango, savanna mahogany, red onion, alkanel, al, Zobo, Annato, cannas etc.

Animal Origin

Natural substances such as carminic acid, kersmesic acid and laccaic acid (popularly known as lac dye) obtained from exudation of dried bodies of insects namely: cochineal, kermes, kerrialacca (kerr) respectively are well known and used for dyeing purposes from ancient times(Grierson, 1989). These acids find limited use for colouring food materials and cosmetics. Some examples of animal dye sources include; the urine of cow, camel dung, shellfish, Mollusc etc.

Mineral Dye: The most commonly used mineral is Geru (Redchre) known for its characteristic shade. Oxides of iron, tin, bismuth and antimony have been used along with vegetable or insect

dyes to obtain the desired shades on fabrics as mordants which not only helps in dye molecules adherence but also gives a gamut of colours with a dye.

Advantages of Natural Dyes

Natural dyes have certain characteristics, which makes them more generally accepted in the environment. Some of these characteristics are as follows.

- i. Natural dyes are more eco-friendly than the synthetic dyes since the procedures of synthetic dyeing much produces pollutants.
- ii. Carcinogenic components which are highly dangerous are not found in natural dyes.
- iii. Most natural dyes are known as antioxidants
- iv. Clothes dyed with natural dyes are most likely to command higher price in the market because of the aesthetic nature.
- v. Depending on the mordant used, one natural dye can give a variety of colours which also depend on the source of the dye. A dye may obtain 4-14 different colours and shades.
- vi. Natural dyes are derived from natural sources unlike the synthetic dyes
- vii. Though all natural dyes are not 100% safe, they are less toxic than their synthetic counter-parts. Many of the natural dyes like turmeric, annatto and saffron are permitted as food additives. Many natural dyes have pharmacological effects and possible health benefit.
- viii. Natural dyes are obtained from renewable source unlike synthetic dyes.
- ix. Natural dyes causes no disposal problems as they are biodegradable
- x. Practically no or mild reactions are involved in their preparations.
- xi. Many natural dyes have the advantage that even though they have poor wash fastness rating, they do not stain the adjacent fabrics in the washing process because of the non-substantive nature of the dye toward the fabrics (Eforia, 2010). An exception to this is turmeric, which shows substantivity for cotton.

For successful introduction of natural dye into technical dyeing process some additional demands have to be fulfilled. These are:

- i. increase the number of available natural dyes with acceptable fastness properties suited for one-bath dyeing process.

- ii. formation of an efficient supplier organization which is able to provide a dye house with standardized dyes of constant quality and to generate an inventory of suitable natural dye from application point of view.
- iii. availability of technical information about the use of the dyes collected from forest or locally grown plantation. Emphasis should be made on production of plant materials in sufficient amount with modern agricultural methods which would include simple and environmentally clean extraction methods suiting the requirement of a dye house.
- iv. determination of biodegradability of the waste generated after dye extraction from plant sources.

2.2.2.2 Drawback of Natural Dyes

Natural dyes are considered to be eco-friendly for dyeing textile materials especially natural fibers. However, there are many limitations in the usage of natural dyes. Some of these limitations are:

i. Tedious Application Process

Natural dyes required a longer dyeing time in comparison with synthetic dyes as in most cases, an additional mordanting step is required. Use of raw dye-bearing material ensures authenticity but at the same time involves additional dye extraction steps that requires time and separate set-up. Natural dyes in this form are not suitable for use in many commercial dyeing machines which makes the process labour intensive. Exhaustion of most of the natural dyes on textile material is poor in spite of using the mordants which leaves a large amount of dye molecules in the dye bath after –dyeing.

ii. Limited Shade Range

The shade range of natural dyes is limited. Red and yellow which are examples of primary colours have several sources but blue which is also a primary colour has only one source. As natural dyes differ in their applications process, only few dyes can be applied in mixtures and differences in fastness properties further limit the choice.

iii. Non Reproducible Shades

Difficulty in reproducing the shade is another major drawback of natural dyes which is caused by the inherent variations in the proportion of chemical constituents in the natural material and thus in its crude extract depending upon the maturity, variety and agroclimatic variations such as soil type, region, etc. Therefore, it is extremely difficult to produce the same shade with a particular natural dyes in every dyeing operation.

iv. Fastness Properties

Colour fastness to light and washing are most important parameters used to evaluate or ascertain the performance of a textile and deciding about its end use. Although, colour fastness to rubbing and perspiration are also important especially if it is to be used as apparel. A material should have good fastness to light if it is to be used for making curtains although a little lower fastness to washing may be satisfactory for this application.

v. Safety Issues

Exploration of new sources for dyes certainly helps in increasing the shade range of natural dyes with good fastness properties. However extensive research on the safety of these materials to human and the environment would be needed before propagating their usage as everything from natural origin may not be safe. This is because some substance from nature are poisonous.

Therefore thorough toxicological evaluation for the new sources are necessary. Use of metallic mordants also requires caution so as not to cause adverse health effects during handling.

2.3. Natural Dyeing Principles

Application of natural dyes in today scenario makes use of modern science and technology not only to review the traditional technique but also to improve its rate of production, cost, effectiveness and consistency in shades. It therefore requires some special measures to ensure evenness in dyeing. Many factors have to be accounted for when one works with natural dyes. They are as follows.

2.3.0 Nature of Material to be Dyed

Animal proteins like wool and silk dye are best in acidic conditions and are weakened by alkaline. If an animal protein is dyed in alkaline condition, it is best to end with a diluted vinegar rinse to restore a slightly acidic pH to the fibre before they dry. Plant materials like cotton dyed best in alkaline conditions and are weakened by acids. If cotton is dyed in acidic conditions, it is best to end with weak washing soda bath to restore the fibers to slightly alkaline before they dry.

2.3.1 Temperature

Different dye shows different characteristics at different temperatures. Most plant dyes shows optimum performance when being heated (i.e madder) but changes colour if allowed to boil. Sappan wood also has a tendency to change colour when heated for prolonged hours. Some dyes work best at lower temperatures (safflower and woad/ indigo).

2.3.2 Agitation

In order to achieve even dye uptake, one should move the fibre around as much as possible in the dye bath. Unfortunately, when wool is heated and agitated, it tends to felt. So one must be very careful about how much one should move it round. For most wools, heating and cooling the dye – bath slowly and being gentle while moving the fibres is necessary to avoid felting.

2.4 Mordanting

A mordant is a chemical that when heated with the fibre, attaches itself to the fibre molecules. The dye molecules then attaches itself to the mordant.

Different mordants give different colours when combined with the same dye. For example, the dye cochineal when used with alum sulphate gives a fuchsia colour, when used with tin the colour is more scarlet and when used with copper, it is purplish. Mordants, except for alum and iron are considered toxic and therefore should be avoided in the preparation of eco-textile, otherwise the whole exercise will be self defeating. As such mordants are toxic, the disposal of the bath becomes an environmental problem. Therefore the choice of mordants is limited. Only alums and iron are ideal safe mordants.

Different Mordants and Methods of Mordanting

Mordanting can be defined as the application or treatment of textile fabric with metallic salts or other agents that can form complex which fixes the natural mordantable dyes onto the textile fabrics. Mordanting can be successful either by pre-mordanting, simultaneously mordanting and post mordanting. Various types of mordants can be applied on the textile materials to derive different colours or shades, to increase the dye uptake and to enhance the colour fastness characteristics of any natural dye (Paul *et al.*, 2002).

The effect of copper tetraoxosulphate (vi) and potassium heptaoxodichromate (vi) on colour fastness features of cotton, silk and wool were studied by Dayal *et al* in 2006. The metal ions such as Fe(II), Cu (II), Sn(II), Cr(VI), Al(III) was used to treat wool and was used to dye with beet sugar colourant and the result showed that this dyeing is capable of withstanding the fastness standard requirements (Mathur *et al.*, 2001).

Optimization of the different concentration of mordants was reported by Agarwal *et al.*, (1993). They reported that the optimum shade can be produced by 0.08% of Copper sulphate, 0.06% of potassium dichromate, 0.04% of ferrous sulphate and 0.15% of alumon mulberry silk fabric.

Aqueous methanol was used to extract natural dyes from teak plants leaves which produced brick red colour on wool and silk in the presence of varying mordants. (Nandal, *et al.*, 2001). Regardless of the method of mordanting, silk treated with potash alum showed an elevation in colour fastness properties when exposed to sunlight for test. Those treated with copper sulphate, ferrous sulphate and potassium dichromate indicates good to excellent fastness properties (Mahale *et al.*, 2003). Turmeric was used to dye wool yarn under different concentration of natural mordants and chromium also using similar mordanting conditions, and similar colour fastness was seen (Mathur *et al.*, 2001). Extract from tulsi leaf when applied on fabrics with or without mordant produced pale to dark green with excellent fastness. Silk produces lower shade depth when mordanted with magnesium sulphate. But when mordanted with copper sulphate, a higher depth of shade was produced (Mauliket *et al.*, 2005).

Different metal sulphates and its effects as mordants were also studied and it was reported that the dyeing depth can be enhanced using different metal salts as mordants. The pre-mordanting and post-mordanting by using aluminum sulphate and ferrous sulphate improves and makes the

colour to be better in terms of light fastness uptake and colour retention on repeated washing (Das *et al.*, 2006). Though, the application of such mordant does not enhance wash fastness characteristics of the substrates of dyed textile with pomegranate. Also, aluminum sulphate and ferrous sulphate enhances colour retention on washing and thereby enhance the fastness properties for substrate of dyed fabric with tea leaves. Chan carried out a study on wool dyeing using four varieties of tea (Chan *et al.* 2000). Protein fibres that are coloured now becomes blackish when ferrous sulphate was used as mordanting agent.

The route followed in pre-mordanting favours jute dyeing (Samanta, *et al.*, 2003) with direct dyeing using aluminium sulphate as a mordant. But simultaneous mordanting route ends up with a better result for madder on cotton fabric using the same mordant. The use of aluminum sulphate and alum as mordants has been advocated since they are more eco-friendly.

Various types of mordants and mordanting methods actually affects the extent and rate of photofading. High resistance to fading is mostly noticed when ferrous sulphate is used while reverse is the case when stannous chloride or alum is being used.

On the other way round, enhancement of light fastness is noticed when post mordanting is carried out with copper or ferrous ion while pre-mordanting attains climax if stannous chloride or alum is used (Gupta *et al.*, 2004).

2.5 Conventional and Non Conventional Methods of Natural Dyeing

2.5.1 Conventional Dyeing

Based on the chemical nature of a natural dye, dyeing can be carried out in an acidic bath, alkaline bath or using a neutral bath. Different reports are seen on various mordanting methods as well as dyeing methods of various textile fabrics. For instance, dyeing of silk and cotton with babool, indigo, heena, marigold, tesu etc with various mordants are reported. Through the use of different mordants, different kinds of shades like brown to black, orange to yellow and yellow to green can be obtained (Mohanty *et al.*, 1987). Notwithstanding, the fabrics to be dyed has to be bleached, scoured or treated using chemicals before dyeing could take place. Therefore, state-wise and source-wise, various artisan dyers, manual skilled dyers and professional dyers are performing natural dyeing of cotton, silk and wool for a very long time and have come up with

some special approach or techniques and processes for individual dye-fabric combination to obtain a particular shade.

A very good example of conventional dyeing practice is practiced in Maharashtra in India (Mohanty *et al.*, 1987). In this method, the fabric firstly prepared by dunging, washing, bleaching and steaming followed by alkaline lye and rinsing. The fabric is then immersed in a solution of harda/myrobolan and then sun dried. The fabric is then premordanted by soaking it in a solution of water and alum. Paste of tamarind seed or gum is added to make it sticky in some places. For dyeing to therefore take place, the fabric is wholly boiled with an extracted aqueous solution of a particular natural dye until all the colouring matter is fully assimilated by the cloth. The dyed fabric is then washed rinsed and spread out for drying in air under a moderate sunlight. In order to brighten the colour, water is sprinkled at certain intervals on the fabric surface. This could be done for 3-4 days for efficient result. If necessary the fabric is starched by immersing it in a paste of wheat or grain flour or in a solution of babool gum and then sun dried.

2.5.2 Non Conventional Dyeing

The need and demand for ecofriendly dyes has led to the reawakening of natural dyes for textiles, with a better energy, efficient process of dyeing and better reproducible shade developing process.

It has been reported that neem leaves gives a better dye uptake by using the conditions of ultrasonic energized dyeing. This condition gave rise to uniform dyeing, better wash and light fastness on natural fabric like cotton (Senthikumar *et al.*, 2002).

Dyeing under ultrasonic conditions has been found to be preferable because it consumes less heat for the same shade. Nylon was dyed with three different natural dyes using different mordants using two different approaches (High temperature, High Pressure (HTHP) and open bath. It was then observed that HTHP dyeing approach was better than open bath approach. (Lokhande *et al.*, 1999).

This non-conventional methods can also be carried out using microwave and sonicator. This approach is highly eco-friendly (Vankar *et al.*, 2007). Also, dyeing can take place in supercritical carbon dioxide fluid and this method is highly advantageous compared to aqueous liquid

extraction. The supercritical carbon dioxide is relatively rapid process because of high diffusivities and low viscosities associated with carbon dioxide fluids.

Notwithstanding, due to high cost, ignorance and limitations on the side of the small scale dyers, these methods are not efficiently employed. None of them has yet been put in place commercially.

2.6 Colour Fastness Properties of Natural Dyed Textiles

The resistance of a material to change in any of its colour features or characteristics or the extent of transfer of its colourants to an adjacent white material in contact is regard as colour fastness. Colour fastness can be assessed using the standard grey scale or by loss of depth of colour in original sample. The major fastness properties considered for all textiles are light fastness, rub fastness and wash fastness.

2.7 Standardization of Natural Dyes

Natural dyeing has the problem of standardization. In 1971, Rita Adrosko wrote about vegetable dyes in “Natural Dyes and home Dyeing”. Craftsmen are becoming increasingly enthusiastic about this out-dated and time-consuming process for one of the reasons that manufacturers rejected it because of difficulty of standardization.

Natural dyestuff produces a particular kind of colour. No two dyestuff are identical because each have little differences due to impurities peculiar to the particular plant material used.

The concentration of colourants in a plant varies. Not only do the variation occur between plants of the same species, but also from part to part of the same plant so that for instance in madder, the dye is contained in roots not the leaves. The type and quantity of chemicals present are affected by such things as soil species, whether time of harvest, as well as the part of plant used. The manner in which they are stored and processed also has a profound effect. Colour varies greatly with plants grown in different areas due to mineral content of the soil and various other factors of growth.

In an effort to standardize colours, dye plants were often cultivated rather than gathered wild. Many were grown commercially. In order to get a standard colour from a particular species of

dye plant 400 years ago the farmer worked empirically by selecting and cultivating plants that produced a dye that got closer and closer to the colour he wanted. He also tried growing the plants under different conditions to see what type of soil gave the best result. When he reached his goal, he then maintained the results by always growing the same species under the same conditions using colour as his control. By keeping good records and adjusting the variables he learned by experience how to obtain the desired colour but it wasn't easy or exactly the same each time. Even today, it is not possible to precisely match colour from batch to batch not even with synthetic dyes (Cannon, 2002).

2.8 Description of Plants Used for the Research

2.8.1 *Berlinia grandiflora*

Berlinia grandiflora is an evergreen forest tree that a times is being planted as ornamental tree. It can also provide shades in villages and coffee plantations. It belongs to the family of Caesalpiniaceae. It is a leguminous plant. It is mostly found in Nigeria, Guinea, Mali, Central Africa and Democratic Republic of Congo (*Berlinia grandifloraison* and Dalziel, 1963). In the eastern part of Nigeria (Ibo), this plant is called “ububa” while the Yorubas in the Western part of Nigeria refer to it “apado”.

The sap extracted from the bark of *Berlinia grandiflora* has been reported to be used in the treatment of wounds and sores. The bark decoctions are used for the treatment of hemorrhoids and liver problems (Gill, 1992). The leafy twig can be boiled with water to be used for the treatment of a feverish condition. It can also be used to combat nausea and vomiting. The leafy decoctions can be taken as a tonic (Gill, 1992). The stem bark extract was also reported by Asuz *et al* in 1993 as being used as analgesic to relief pain without inducing unconsciousness. Its extract also shows good properties of antihelminthic and antimicrobial. This plant has a great resemblance with oil bean seed locally called “Ugba” in Ibo language of Nigeria. Hence, in May to July 2013, a high death rate was recorded in Imo State in Nigeria due the consumption of Ugba (Oil bean seed). This is as a result of the dubious act of some persons who mixed oil bean with the seed from the plant of *Berlinia grandiflora* and started selling it for consumption (Vanguard and Daily Independence Newspaper, 2013).

The wood from this tree is used for construction in house building, flooring, planks, joinery and food containers. It is also used for interior trim, ship building, cabinet making, stakes, turnery, drawing boards veneer, railway sleeps, furniture and plywood. The wood is adequately durable because it is resistant to termite attack though vulnerable to pinhole and marine borer attacks.

2.8.2 *Nesorgodonia papaverifera*

This is a species of tree plant which belongs to the family of Sterculiaceae, it is included in the expanded malvacea in the most subsequent systematics. Other common names are. Owoe Kotibe (Ivory Coast), Otutu (Igbo Nigeria), Owoe (Cameroon), Arborbo (Gabon), Kondofindo (Zaire), Naouya (Angola) and Abumana, Epro (Ghana).

The name *Nesorgodonia papaverifera* is translated as “Da” meaning paired and “Nta” meaning double; named after a traditional locally manufactured short gun (Adanta) used by chiefs in the olden days in the eastern part of Nigeria. The buttress root of the wood is the part mostly used in making the butts or the gun. The *Nesorgodonia papaverifera* grows to about 37 m in height, the trunk can reach diameters of 0.8 to 1.0 m over short buttress. It is found in the tropical forest of Africa around Sierra-Leone, Cameroon, Gabon, Ghana and Nigeria. The tree is evergreen or briefly deciduous depending on the location. Its small crown has a flush of pale green in otherwise dark foliage flowers are white and very fragrant. The fruit is woody splitting to release 1 cm long winged seed. It is a strong, heavy attractive red wood. The *Nesorgodonia papaverifera* is fine-grained and hard wearing with medium luster.

It is used for interior and exterior application such as high quality joinery cabinet work, bench tops, boat components, turnery and decking. General construction, flooring, tool handles, gun stocks, plywood and furniture. It is also used for making mortars and pistils.

Thus, from literature survey, no study yet described the use of the two plants (*Berlinia grandiflora* and *Nesorgodonia papaverifera*) as sources of natural colourants.

CHAPTER THREE

MATERIALS AND METHOD

3.1 Materials

The stem bark of *Nesorgodonia papaverifera* was collected from Abbi in Delta State and the stem bark of *Berlinia grandiflora* was collected from Obiaruku in Delta State. The plant materials were identified by Dr. Ebigwai of University of Calabar. Cotton and nylon fabrics were purchased from a local market in Kaduna (Nigeria). Methanol (CH₃OH), Acetone (CH₃COCH₃), Potassium hydroxide (KOH), Ethanol (C₂H₅OH), Silica gel, Chloroform were all of analytical grade and obtained from Sigma-Aldrich chemical company.

3.2 Extraction of Natural Dyes

The bark of *Berlinia grandiflora* and *Nesorgodonia papaverifera* was cleaned with enough water and dried in an oven. The dried bark of the plants was ground into powdered form using an electrical grinder with a steel blade.

The natural dye was extracted from the plant materials using soxhlet extractor. 10g of the pulverized plant material (*Nesorgodonia papaverifera*) was packed and placed in the porous thimble and then placed in the thimble flask in the inner part of the soxhlet extractor. The apparatus was then fitted to flat bottom flask and 250 ml of a chosen solvent was introduced. The Dual purpose flask is then heated gently using heating mantle. The vapour in the DPF then leaves through the by-pass tube and moves straight to the condenser where it is being condensed back to ground state. The condensed vapour (liquid) moves back to the DPF through the siphone tube when the solvent reaches the top. The process automatically repeated itself.

Acetone (250 ml) was used as an extraction solvent to extract natural dye from the bark of *Nesorgodonia papaverifera*. 10 g of the plant material at 20 °C, 40 °C, 60 °C, 80 °C and 100 °C for 1 hour respectively was used for the extraction. A plot of absorbance against extraction temperature was carried out as shown figure 4.11.

Another extraction was done using acetone also as an extraction solvent. In this case, the temperature of extraction was kept constant at 70 °C but the extraction time varies at 1, 2, 3 and 5

hours respectively. A plot of absorbance against extraction time was also carried out as shown in figure 4.12.

These extraction was repeated using methanol, water, methanol + Potassium hydroxide and acetone + potassium hydroxide as extraction solvent. All the extracts of the *Nesorgodonia papaverifera* extracted with the same solvent was pooled together and evaporated to dryness to obtain the extract in paste form.

3.2.1 Thin Layer Chromatography

After the extraction using different solvents with soxhlet extractor, the extract was concentrated and TLC was carried out on to ascertain the actual solvent that will be used for the column. The ratio of the solvents used was 70 – 30 (Chloroform - ethanol).

Precoated TLC plate was developed by taking 1.5 cm from the base to the marginary or starting point line. That line was drawn using a pencil. With the aid of the capillary tube, the emulsified extract was picked using the capillary tube and was introduced into the marginary line and allowed to dry. The TLC tank was developed by mixing 70 ml and 30 ml of chloroform and ethanol which serves as the mobile phase. The reacted mobile phase was transferred into the TLC tank and allowed to stand for 10 minutes so that the tank will be saturated. At the expense of the 10 minutes, the developed TLC plate was introduced into the TLC tank that contained the mobile phase vertically. The TLC plate adsorbs the mobile phase until the mobile phase got to where the sample is spotted. The mobile phase will move the sample from the marginary line (starting point). As a result of gravity, the different compounds contained in the sample will be separated which is the different spots found. R_f of the sample were calculated as to ascertain if the solvent for the mobile phase is okay. At the long run R_f values of 0.8 and 0.9 were obtained from *Nesorgodonia papaverifera* extract. Also, R_f value of 0.79 and 0.8 were obtained for berlinia extract. Hence, the mobile phase (chloroform and ethanol) is okay and can be used for the column.

3.2.2 Column Chromatography

The column was packed using silica gel of mesh 60 – 120 alongside a treated sand. 300 g of the silica gel was introduced into the column that contains a filter (sintered disc). Cotton wool was then introduced. 100 g of the treated sand was also added. Then cotton wool was added again. 2

g of the sample was weighed using analytical balance (Fisher scientific of 0.000 sensitive) and added into the column.

The least polar solvent (chloroform) 200 ml was introduced into the packed column to elucidate. On dropping from tip of the column, 50 ml of the elucidated sample was taken into 4 places. Thereafter, 140 ml of the chloroform was reacted with 60 ml of the ethanol, and was introduced into the same column and elucidated by taking 50 ml into 4 places. After that, the 200 ml analytical ethanol was introduced into the column again and it was elucidated by taking 50 ml in 4 places again.

3.2.3 Final separation

The different elucidated samples were further tested using TLC to ascertain their purity. The two samples, however gave one spot each with R_f values of 0.8 and 0.9 respectively.

3.3 Characterization

The techniques employed for the characterization of the purified dye extracts were Infra-Red (FTIR-8400S) using KBr pellets, mass spectroscopy (GCMS-QP 2010 model), UV-visible spectrophotometer which were carried out at NARICT Research Institute Zaria, ^1H NMR and ^{13}C NMR (Agilent-NMR-Vnmrs 400) at Central Science Laboratory, OAU Ile-Ife. The procedure for all these analyses must be provided.

3.3.1 Infra – Red Experimental Procedures

The procedures used to carry out the analysis in the laboratory are as follows:

1. The computer was turned on and signed in
2. The power was tuned on to complete initialization process
3. The sample holder was cleaned with acetone
4. The spectrum software was launched on the desktop
5. The instrument was set up using set-up button. The sample name, scan range (200 – 4000 cm^{-1}), and scan number was added.
6. The background button was clicked to collect background information of the sample holder.

7. The sample was placed on the sample holder and the button of “Apply” and “start” was clicked to collect the spectrum.
8. Data processing was carried out by labeling the peak using “view” button and “label cursor”. Then the data was saved using “save as” button.
9. The software was the turned off, and the computer was logged off.

3.3.2 Ultra Violet Visible Experimental Procedures

The procedures used to carry out the analysis in the laboratory are as follows;

1. The appropriate sample holder was fitted in the equipment.
2. The UV- visible machine was then turned and the blinking light on the button goes to a stable green colour.
3. The computer connected to the U.V was logged on.
4. Cary Win UV was opened from the desktop, the scan button was clicked in order to start the programme.
5. Set up button was clicked to set the experimental parameters.
6. The button of start was clicked, this made the scan to resume.
7. As soon as the scan finished, a pop up came up. This enables to scan another sample.
8. The sample was changed, the sample name on the pop up box was also changed and the procedure was followed again.
9. The UV- visible was turned off by pressing the button of off.

3.3.3 GC/MS Experimental Procedures

The procedures used to carry out the analysis in the laboratory are as follows:

1. The standard used were straight alkanes, aromatic halide alkyl halide, aromatic ether, and alkanes.
2. The console was entered and GC/MSD icon was clicked to open the GC/ MSD.
3. The analysis was then set-up by clicking on the green arrow.
4. The “Ok” and “Run method” button was clicked to begin the GC/MS automation
5. As run progresses, and the approximate 3 minute solvent delay has passed, peaks started appearing in the smaller sub-windows.

6. Useful data were obtained from the sub- windows. The peaks retention time was displayed at the top of the mass spectrum sub window.
7. In the mass spectrum sub- window, a library comparison search was performed by double right clicking the lower – sub- window.
8. The entire spectrum were analyzed to ensure that the snap shot included every peak.
9. As soon as the run was completed, another sample was introduced. The instrument required a few minutes to return the GC oven temperature back to the 40 °C starting point.

3.3.4 NMR Experimental Procedures

The procedures used to carry out both ¹HNMR and ¹³CNMR in the laboratory are as follows:

1. The USERNAME and PASSWORD was used to log in the machine.
2. The standard sample on the machine was changed with the sample to be analysed.
3. The magnet was locked and shimmed to keeps its field constant and stable during the data acquisition. It also makes the magnet to be uniform and homogenous for sample to get a reasonable resolution and line shape.
4. Parameters were set-up and updated by the NMR centre to enable efficient collection of data.
5. Data were then processed spectrum plotted and saved. This step converts data into NMR spectra.
6. The standard sample was then used to replace the analysed samples at the end.

3.4 Dyeing Procedure

A 5 % stock solution was prepared from the plant extract. The dye bath was prepared using a liquor ratio of 1:50 at 2 % shade on the weight of fabric (o.w.f). The volume required from each stock solution was calculated based on the formula

$$v = \frac{p \times w}{c}$$

Where:

P = percentage shade

W = weight of fabric

C =percentage concentration of stock solution

The extracted solution of each of the dye plant was applied to cotton and nylon fabrics with mordants and without mordants under identical conditions. Direct dyeing (i.e. without mordant) was performed to find out whether the extracted dye has affinity for cotton and nylon in the absence of mordant. Scoured cotton and nylon fabrics were cut into several pieces each weighing 1.0 g. Two different dye extracts which are *Berlinia grandiflora* and *Nesorgodonia papaverifera* and two different mordants which includes Potassium dichromate and Stannous chloride were used in the dyeing process. In each case, a few drops of acetic acid (2 %) was added to the dye bath to considerably reduce the amount of metal mordants in the spent bath.

3.4.1 Control Dyeing (Without Mordants)

The pre-treated cotton and nylon fabrics (1.0 g) each were dyed in separate dye baths with each of the dye extracts. The dyeing was carried out without a mordant so as to serve as a control. Dyeing was conducted at a material to liquor ratio of 1:50 using a shade of 2 % on the weight of fabric (o.w.f.). The dyeing was carried out at 85 °C for 1 hour in standard laboratory dye master. After half of dyeing time, 3.0 g/l Sodium sulphate (Na_2SO_4) was added as exhausting agent. At the end of the dyeing time the samples were removed, washed and dried. However, in dyeing with mordants, simultaneous mordanting technique was adopted. The pretreated fabrics were dyed individually in different dye baths containing 10 % on weight of fabric (o.w.f) of mordant and 20 % (o.w.f) of Sodium sulphate. A material to liquor ratio of 1:50 was also used in all the dyeing. Similar procedure was also adopted for all the dyeing as explained above.

3.4.2 Determination of Optical Density (% Exhaustion)

The optical density of the extracted dyes were determined before and after dyeing at the maximum wavelength (λ_{\max}) of each dye using JENWAY 6405 UV/visible Spectrophotometer, The percentage exhaustion was calculated using the expression below:

$$\% \text{ Exhaustion} = \frac{OD_1 - OD_2}{OD_1}$$

Where OD_1 and OD_2 represent the optical densities of the dye solution before and after dyeing respectively.

3.5 Colour Fastness Test

3.5.1 Determination of wash fastness of dyed samples

The dyed specimens of dimension 5 cm x 4 cm were placed between two pieces of undyed white fabrics of the same dimension. Three pieces attached to each were held together by stitching round the edges to make a composite specimen. The composite specimen was agitated with 10 steel balls in a solution made-up of 5 g/l soap and 2 g/l soda ash with liquor ratio 1:50 as stipulated by ISO 3 standards. The washing was carried out at $60 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ for 30 minutes in a launder-o-meter. The composite specimen was then rinsed, separated and dried. The change in colour of the test samples and the staining of the adjacent undyed white fabric *was* assessed with references to the grey scale (ISO 9001 2000 group).

3.5.2 Determination of the light fastness

Strips of the fabrics and the blue wool standards were cut and mounted on a cardboard paper and half portions of the specimens were covered to obstruct the source of light from getting to that portion. The specimens were exposed due south at an angle of $45 \text{ }^\circ\text{C}$ sloping from the horizontal to natural day light for 72 daylight hours. The specimens were then removed after 72 daylight hours and the extents of their fading were assessed in comparison with the blue wool standards.

3.5.3 Determination of Fastness to Dry and Wet Rubbing

Dry and wet rubbing fastness of the dyed samples was tested using a Crock-meter in accordance with ISO 105-X 12:2001 standards. The specimens were placed in the Crock meter which causes a piece of standard white cloth (starch free 96.100 cotton fabric long type) to rub against the colored specimen under controlled condition of pressure and speed. The rubbing fingers were covered with white cloth, both for the dry test and wet test, and slide back and forth for 20 rubbing strokes. The colour transferred to the white cloth is compared with Gray Scale for alteration of colour, consisting of grade 1-5.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results

The results of extractions are presented in the figures below.

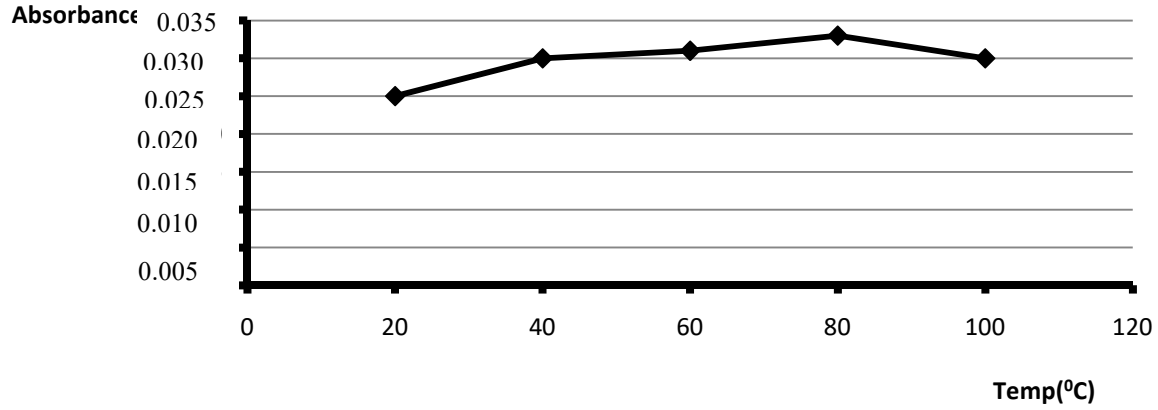


Fig. 4.1: Absorbance of extracted dye concentrations of *Berlinia grandiflora* at different temperatures using acetone as solvents.

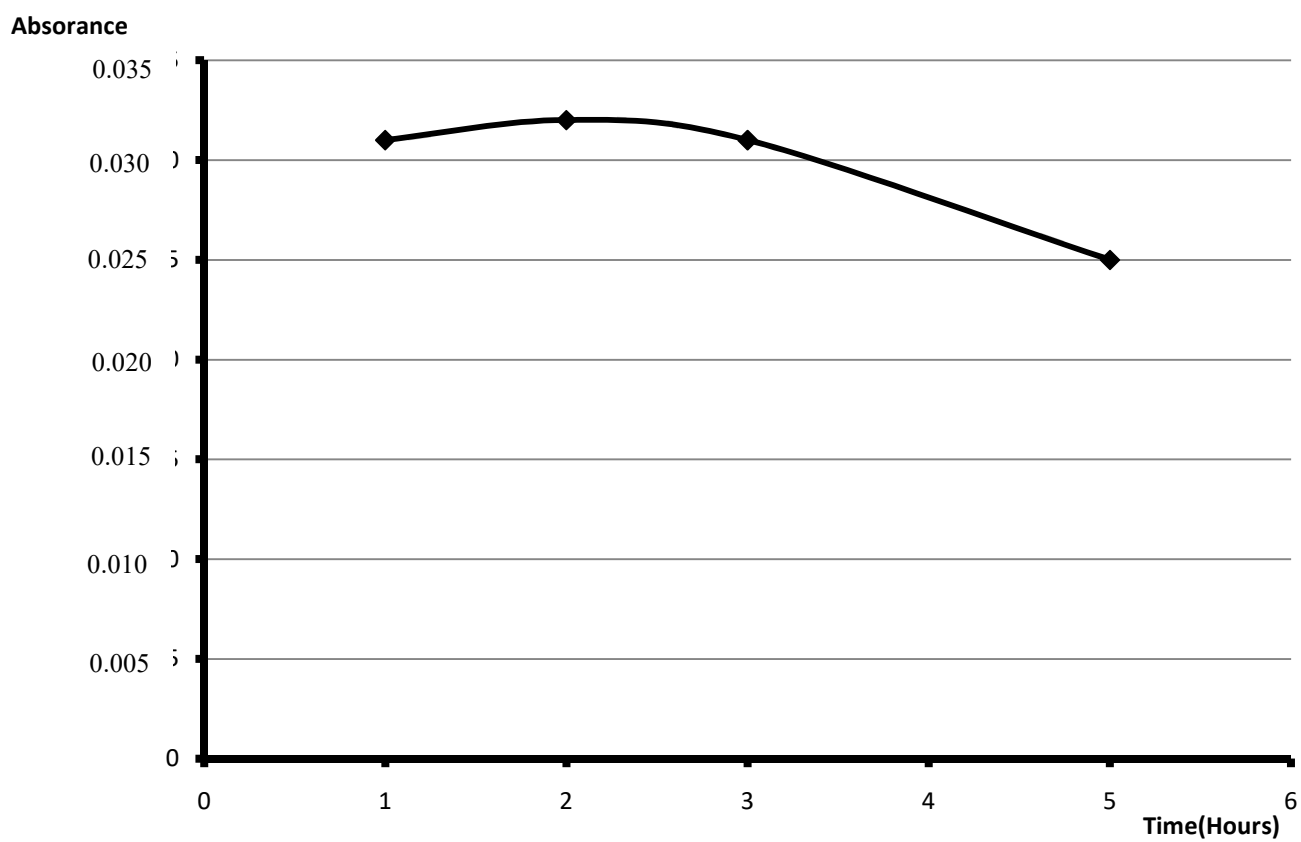


Fig. 4.2: Absorbance of extracted dye concentrations from *Berlinia grandiflora* at different hours using acetone as solvent.

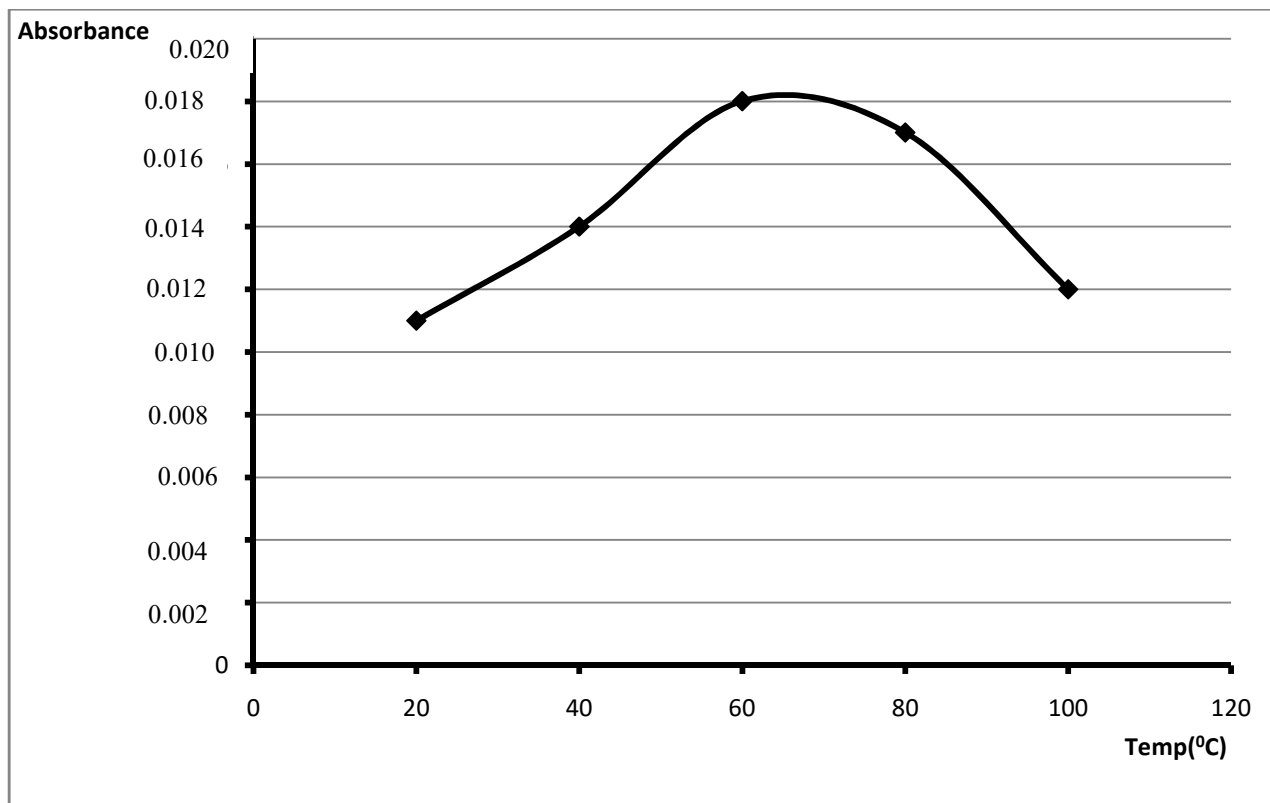


Fig. 4.3: Absorbance of extracted dye concentrations from *Berlinia grandiflora* at different temperatures using methanol as solvent.

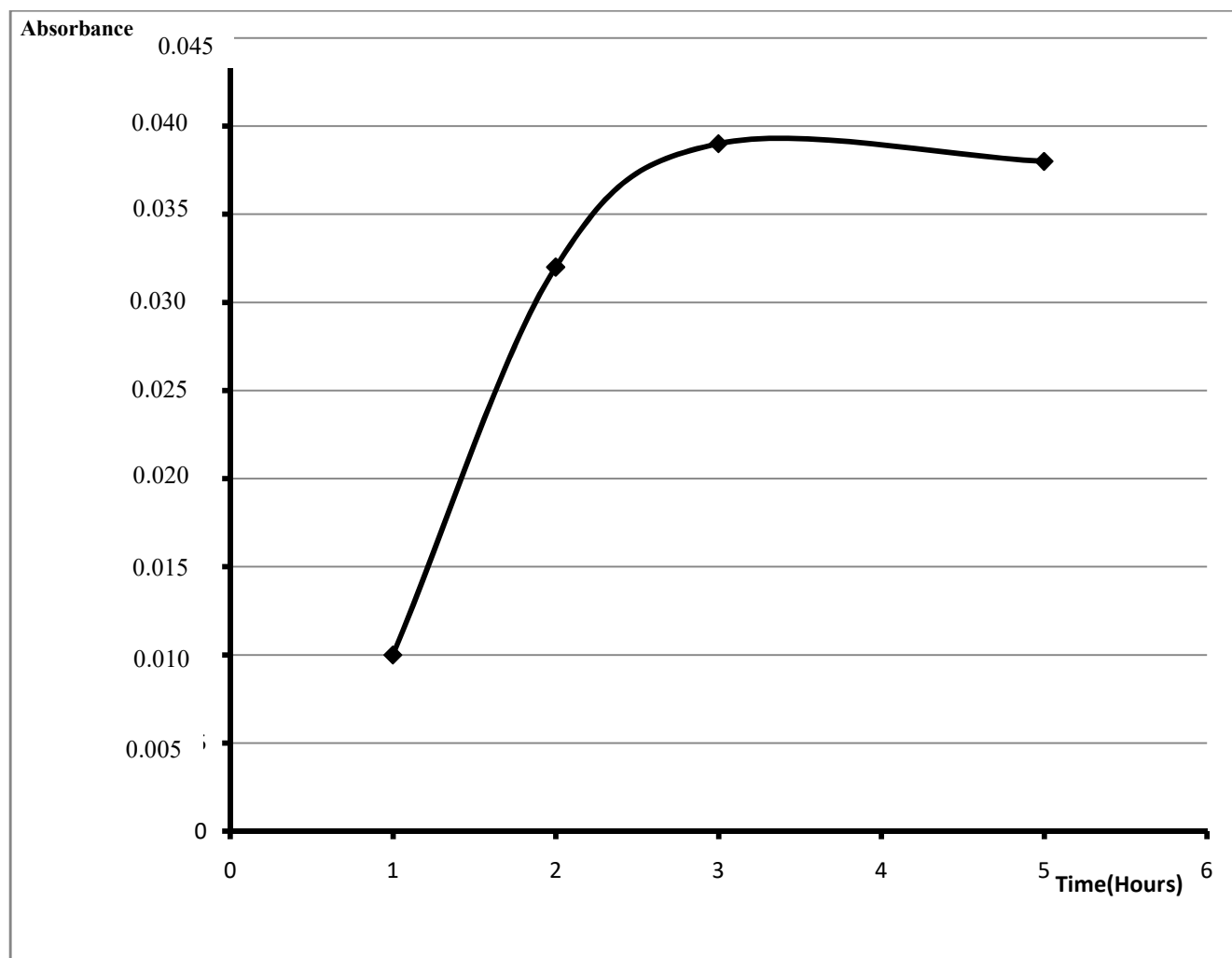


Fig. 4.4: Absorbance of extracted dye concentrations from *Berlinia grandiflora* at a constant temperature of 70 °C using methanol as solvent.

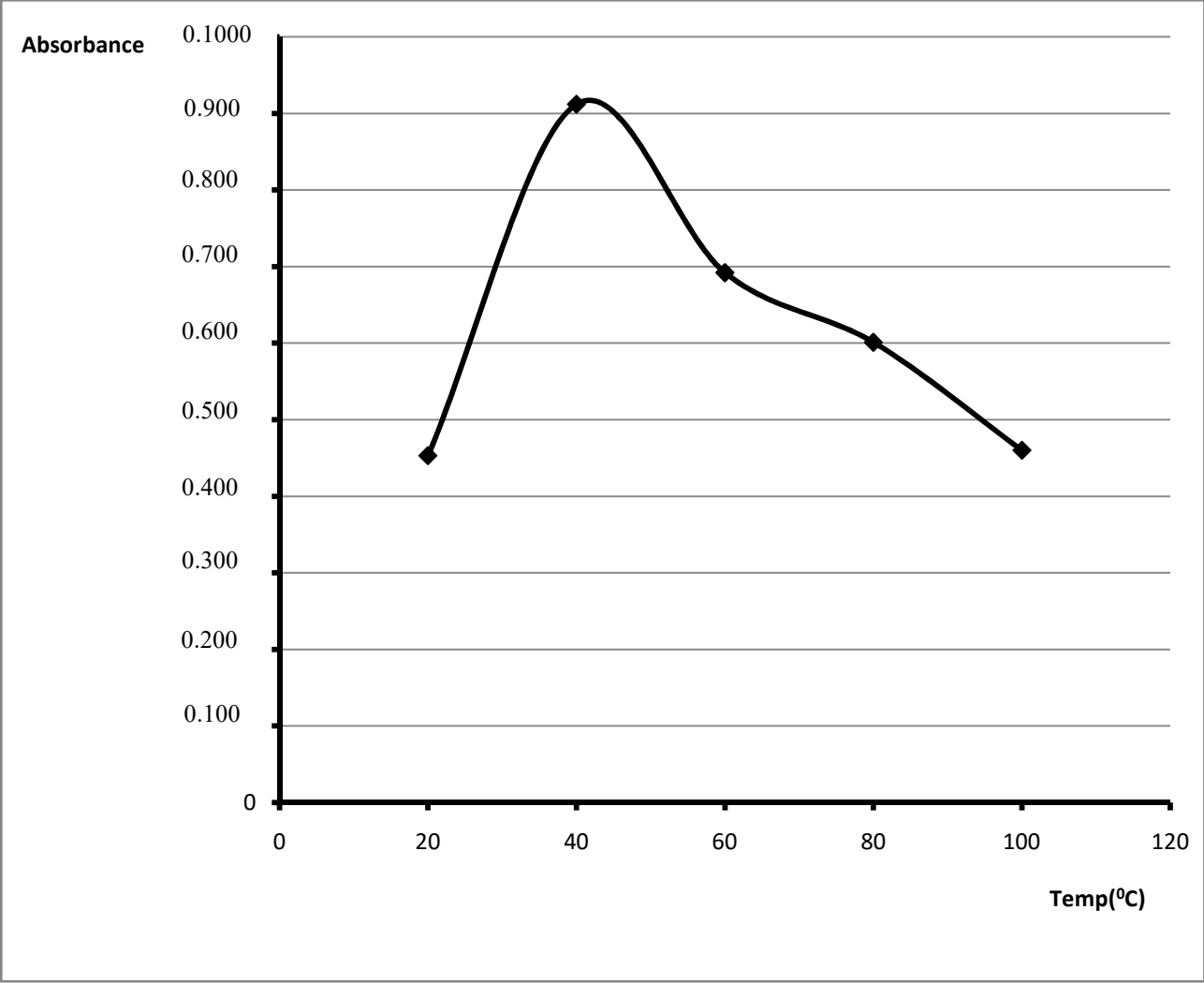


Fig. 4.5: Absorbance of extracted dye concentrations from *Berlinia grandiflora* at different temperatures using water as the solvent.

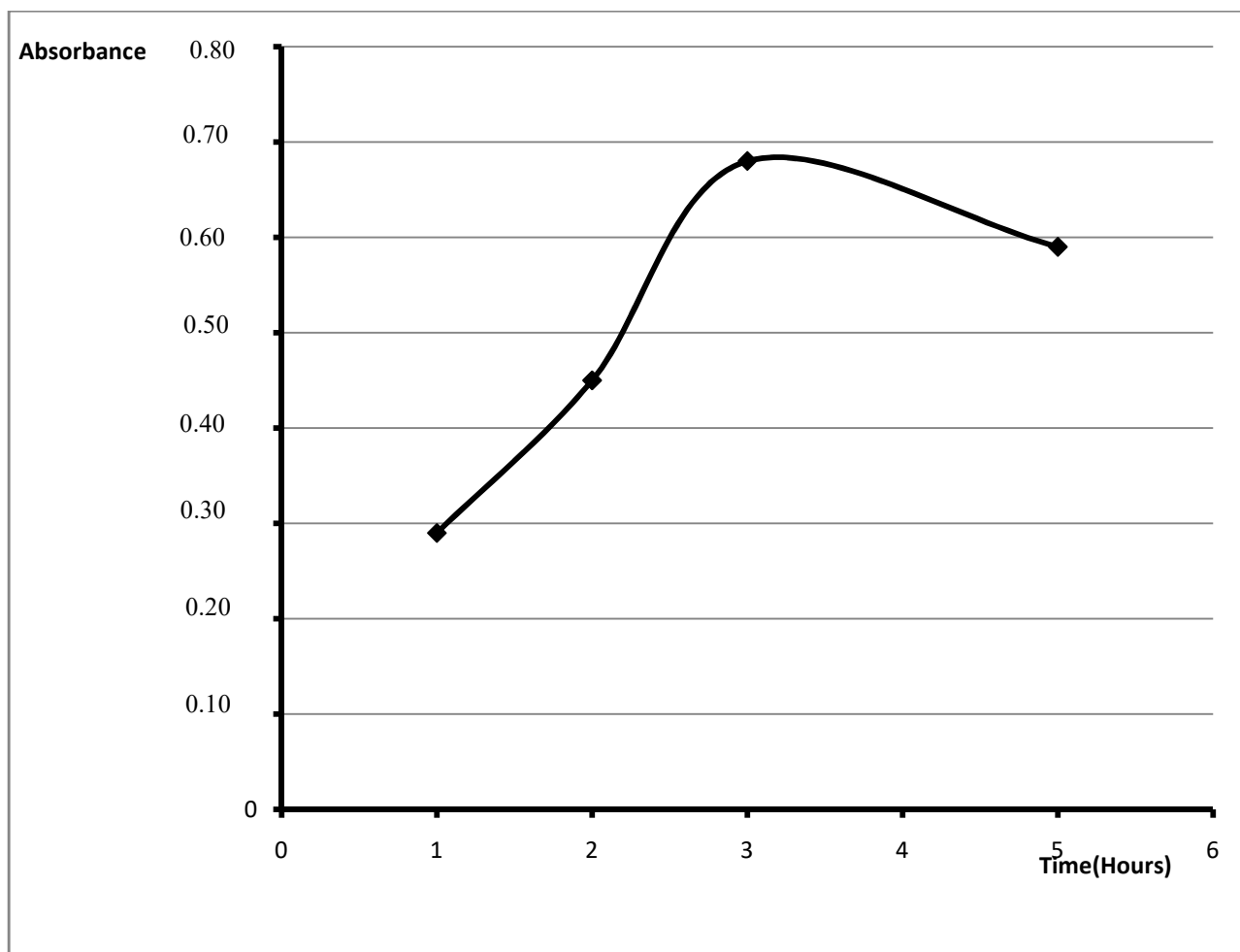


Fig. 4.6: Absorbance of extracted dye concentrations from *Berlinia grandiflora* at constant temperature of 70 °C and various times (hours) using water as a solvent.

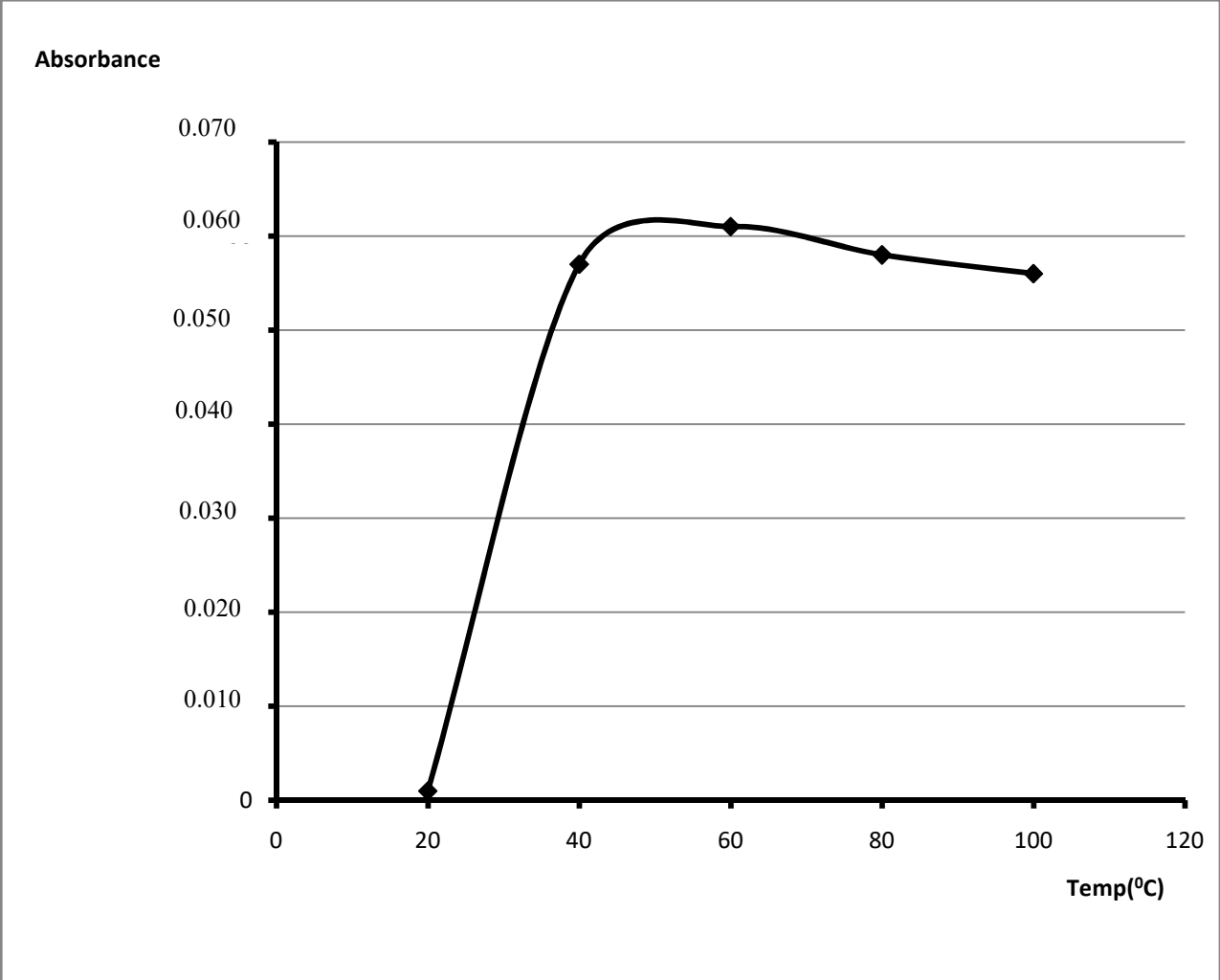


Fig. 4.7: Absorbance of extracted dye concentrations from *Berlinia grandiflora* using mixture of KOH and acetone as solvent at different temperature.

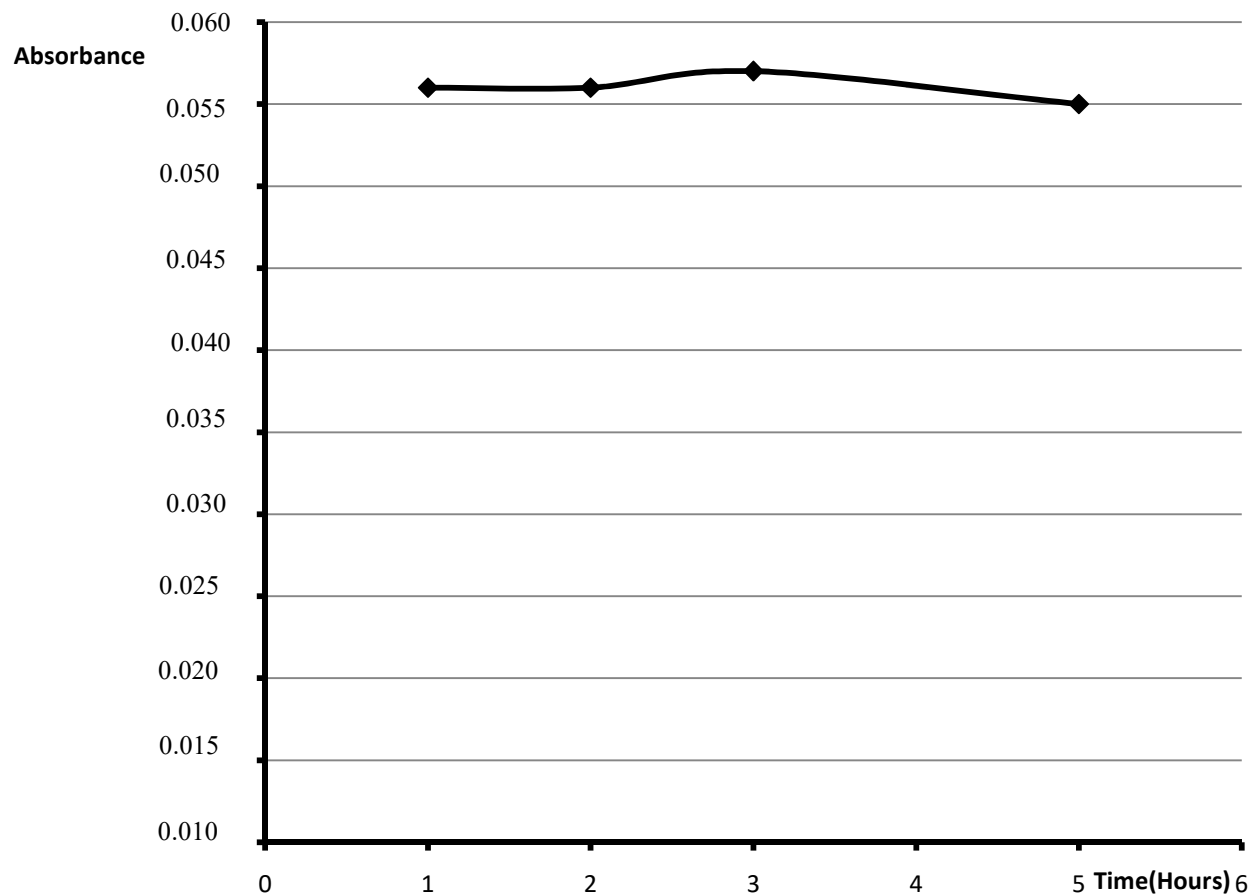


Fig. 4.8: Absorbance of extracted dye concentrations from *Berlinia grandiflora* using KOH + acetone as solvent at constant temperature 70 °C at different times in hours.

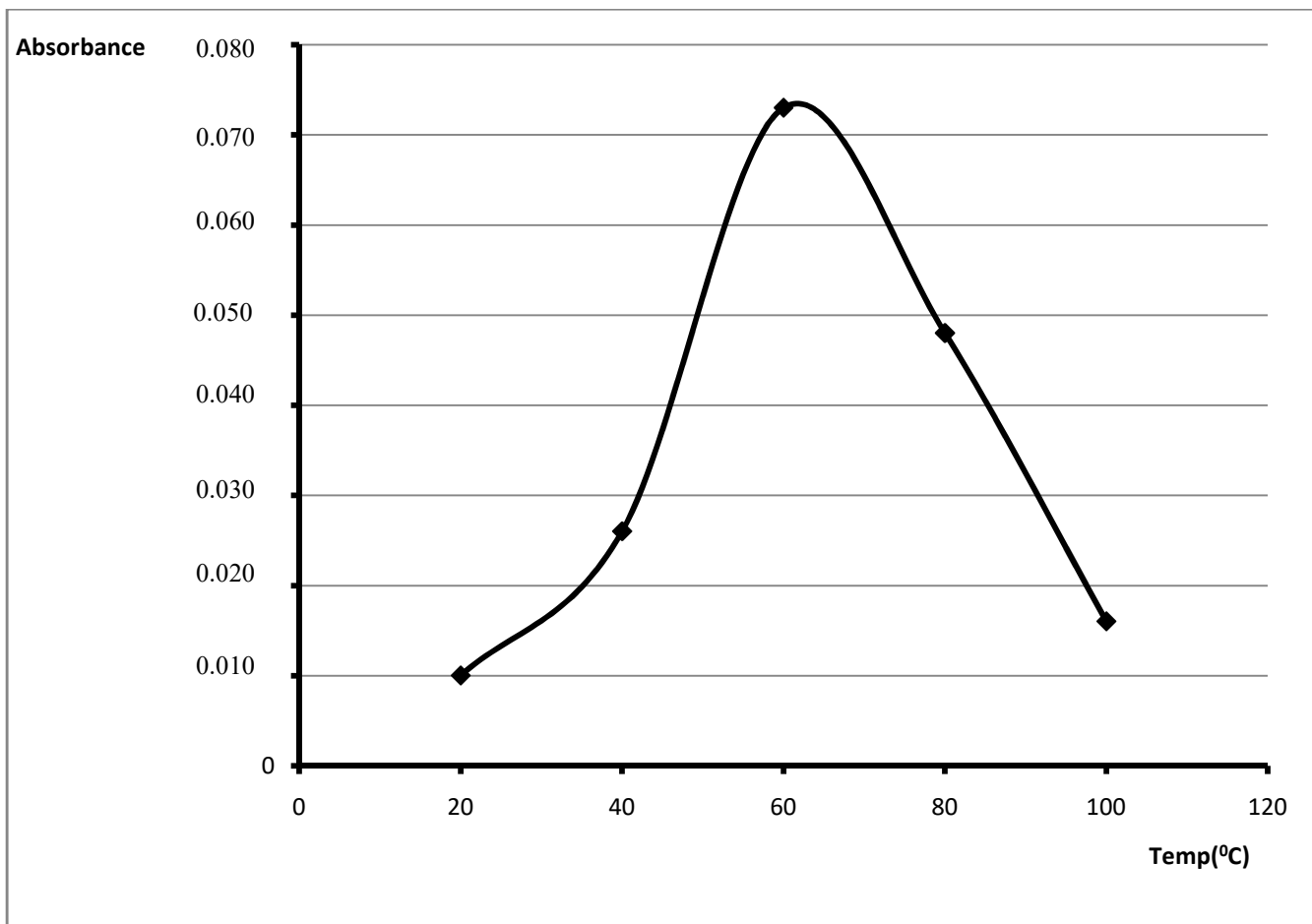


Fig. 4.9: Absorbance of extracted dye concentrations from *Berlinia grandiflora* using KOH + methanol as solvent at different temperatures.

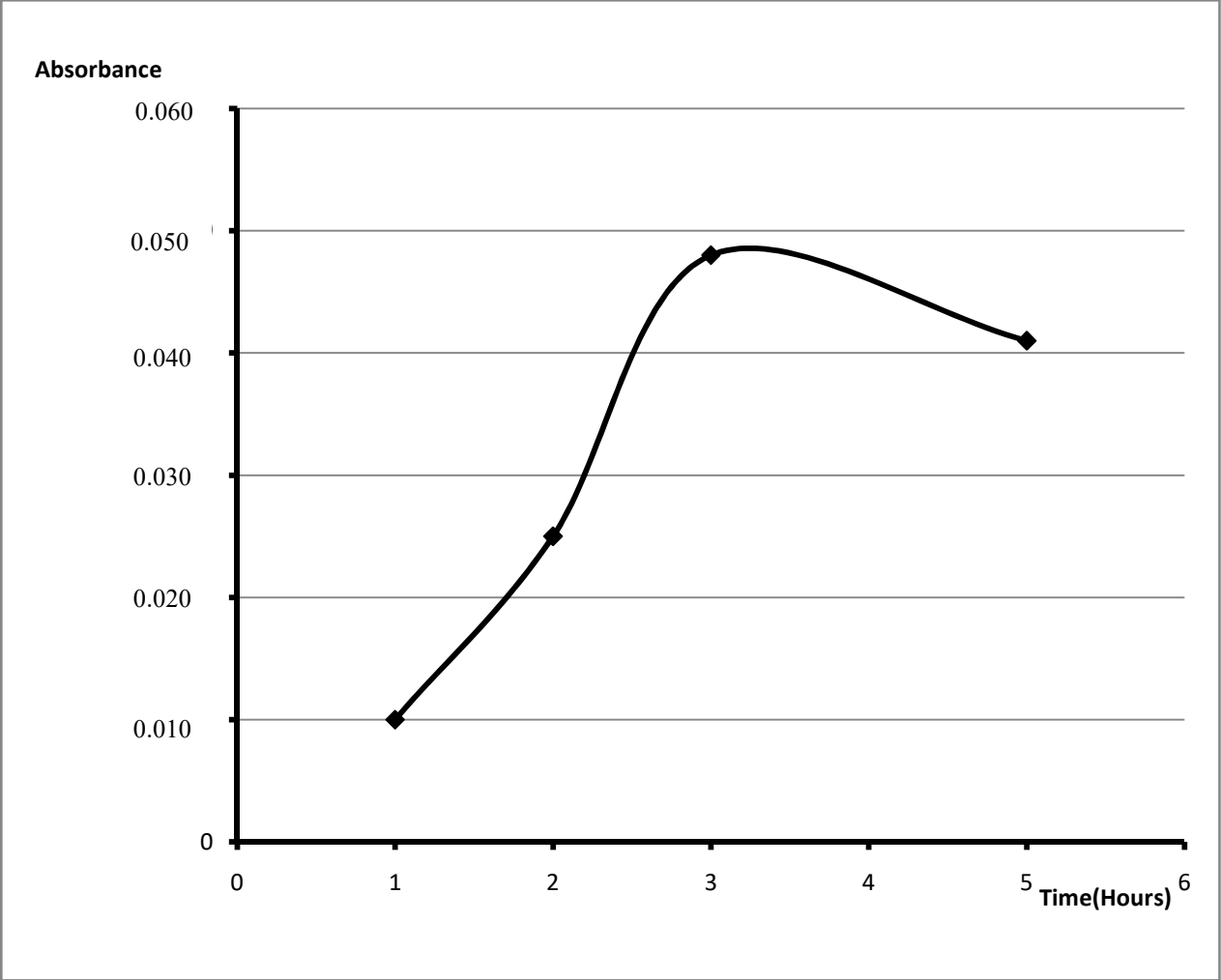


Fig. 4.10: Absorbance of extracted dye concentrations from *Berlinia grandiflora* using KOH + methanol as solvent at a constant temperature of 70 °C

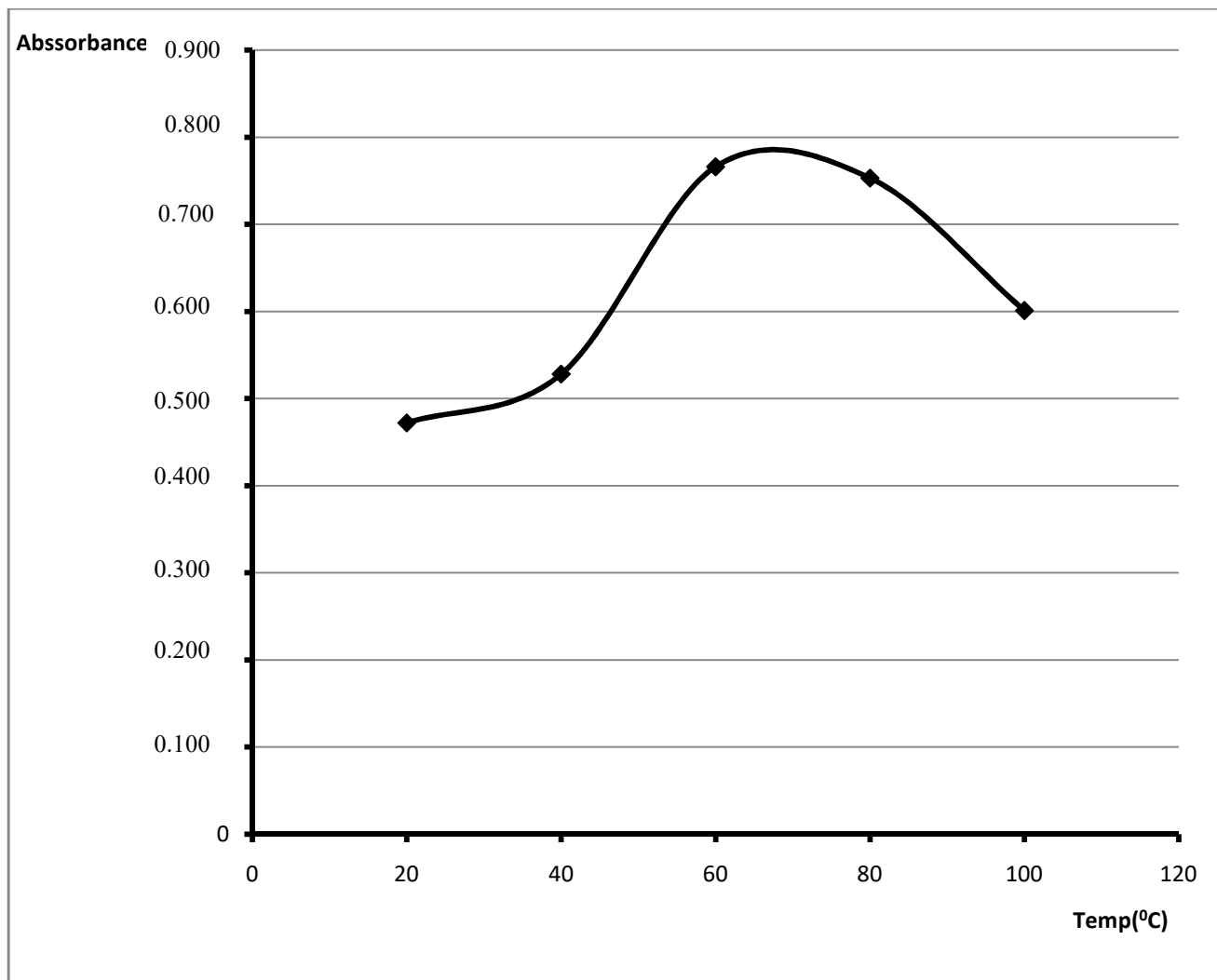


Fig 4.11: Absorbance of extracted dye concentrations from *Nesorgodonia papaverifera* at different temperature using acetone as solvent.

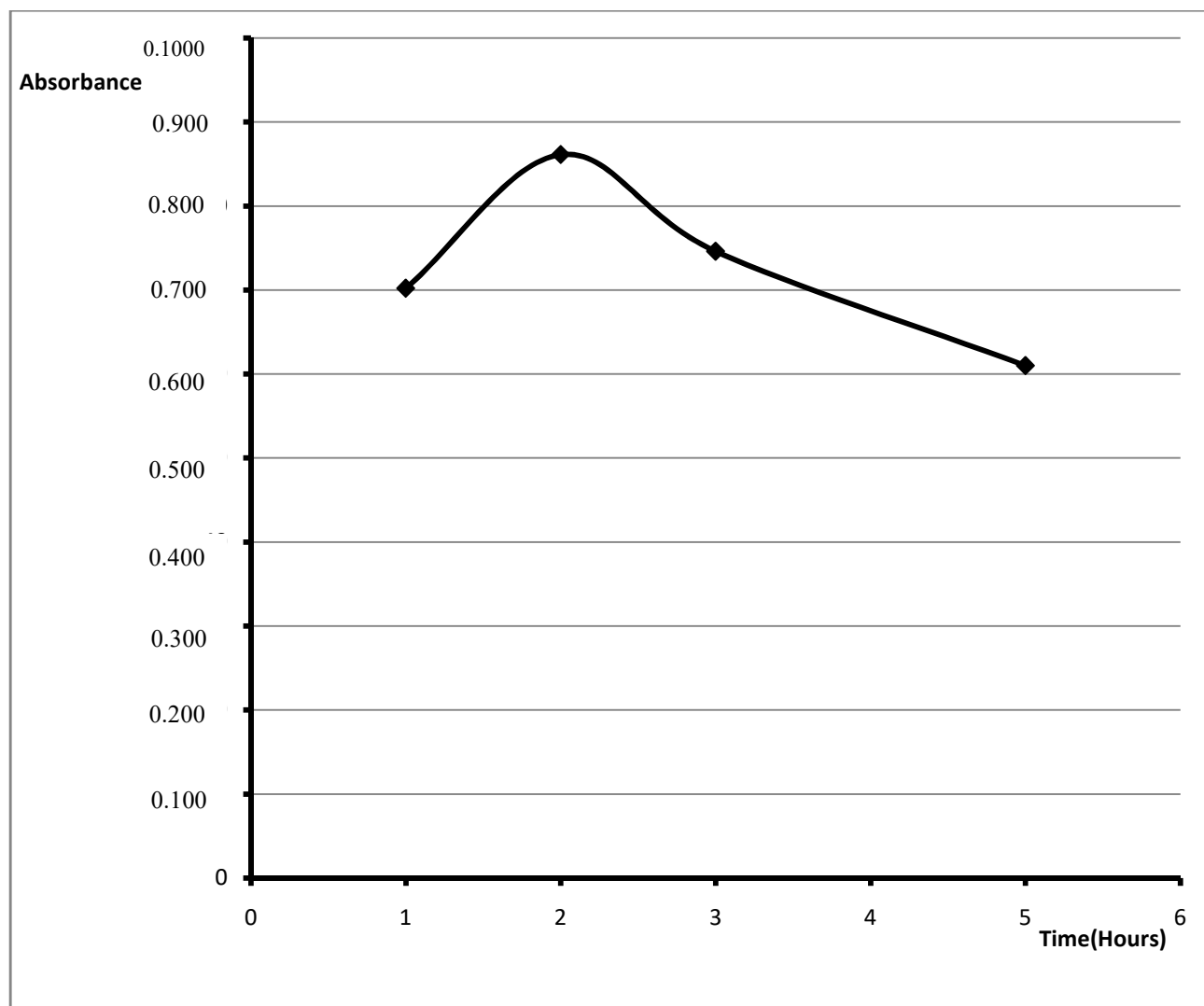


Fig. 4.12: Absorbance of extracted dye concentrations from *Nesorgodonia papaverifera* at constant temperature of 70 °C using acetone as solvent at different time.

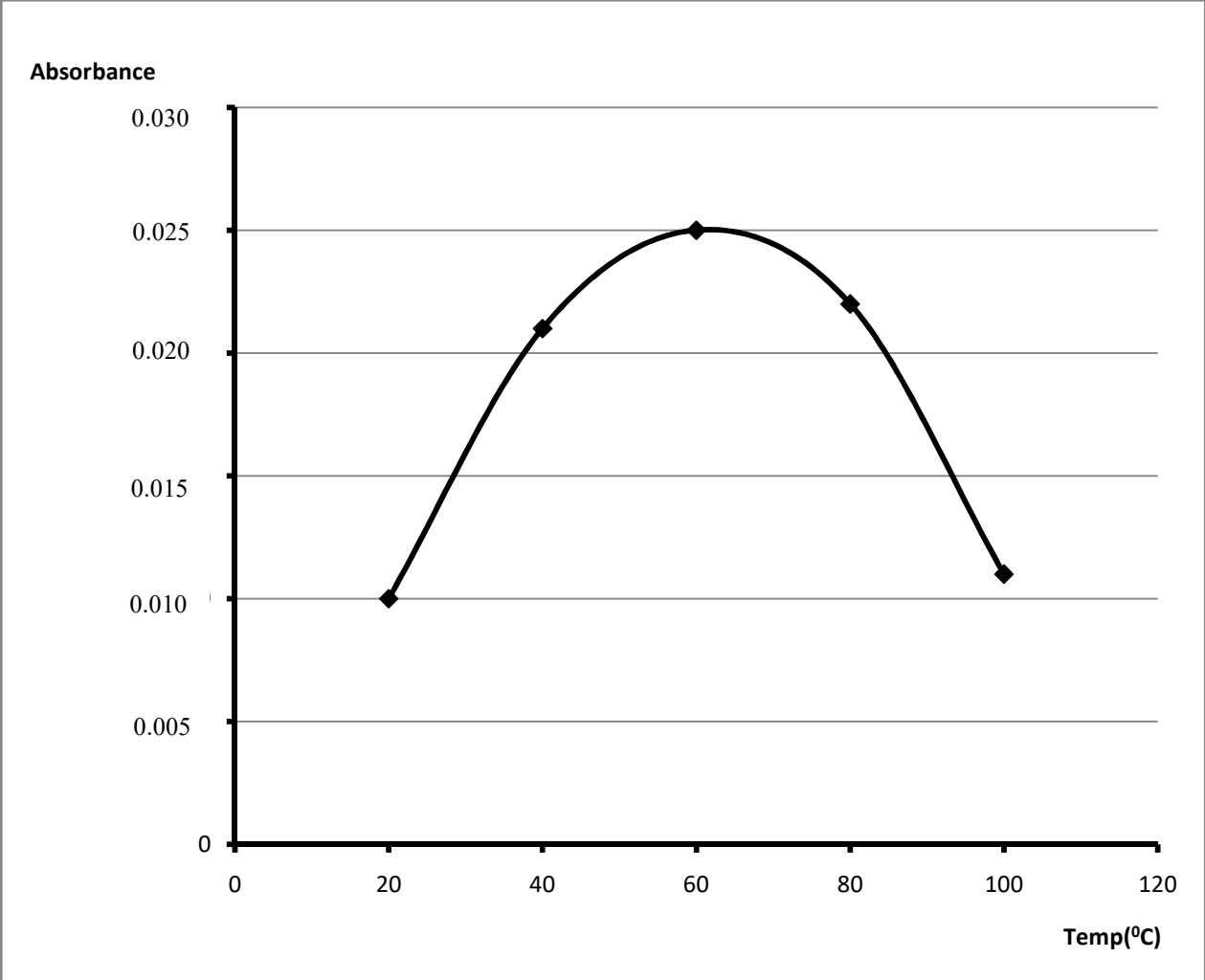


Fig. 4.13: Absorbance of extracted dye concentrations from *Nesorgodonia papaverifera* at different temperature using methanol as solvent.

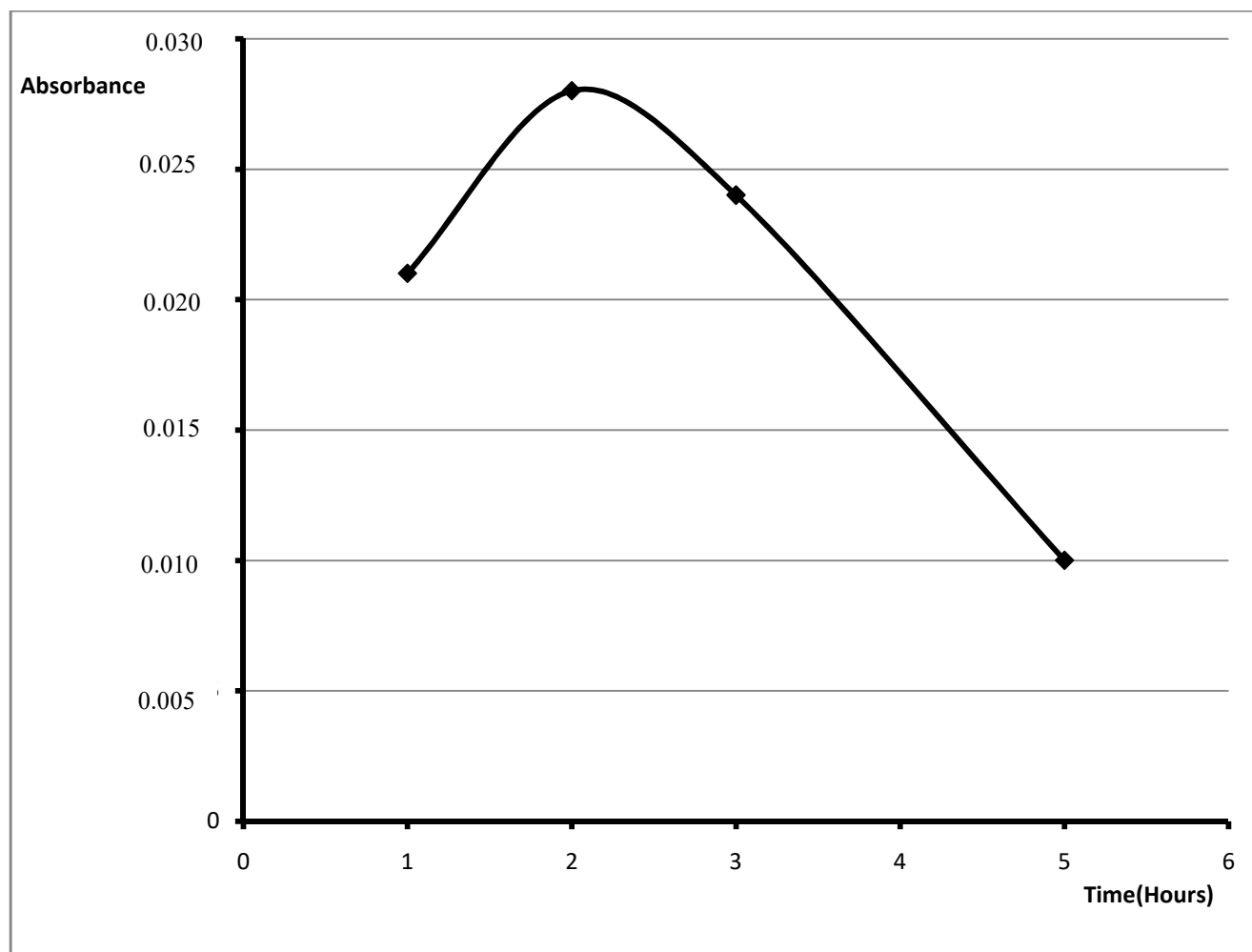


Fig 4.14: Absorbance of extracted dye concentrations from *Nesorgodonia papaverifera* at constant temperature of 70 °C using methanol as solvent at various times in hours.

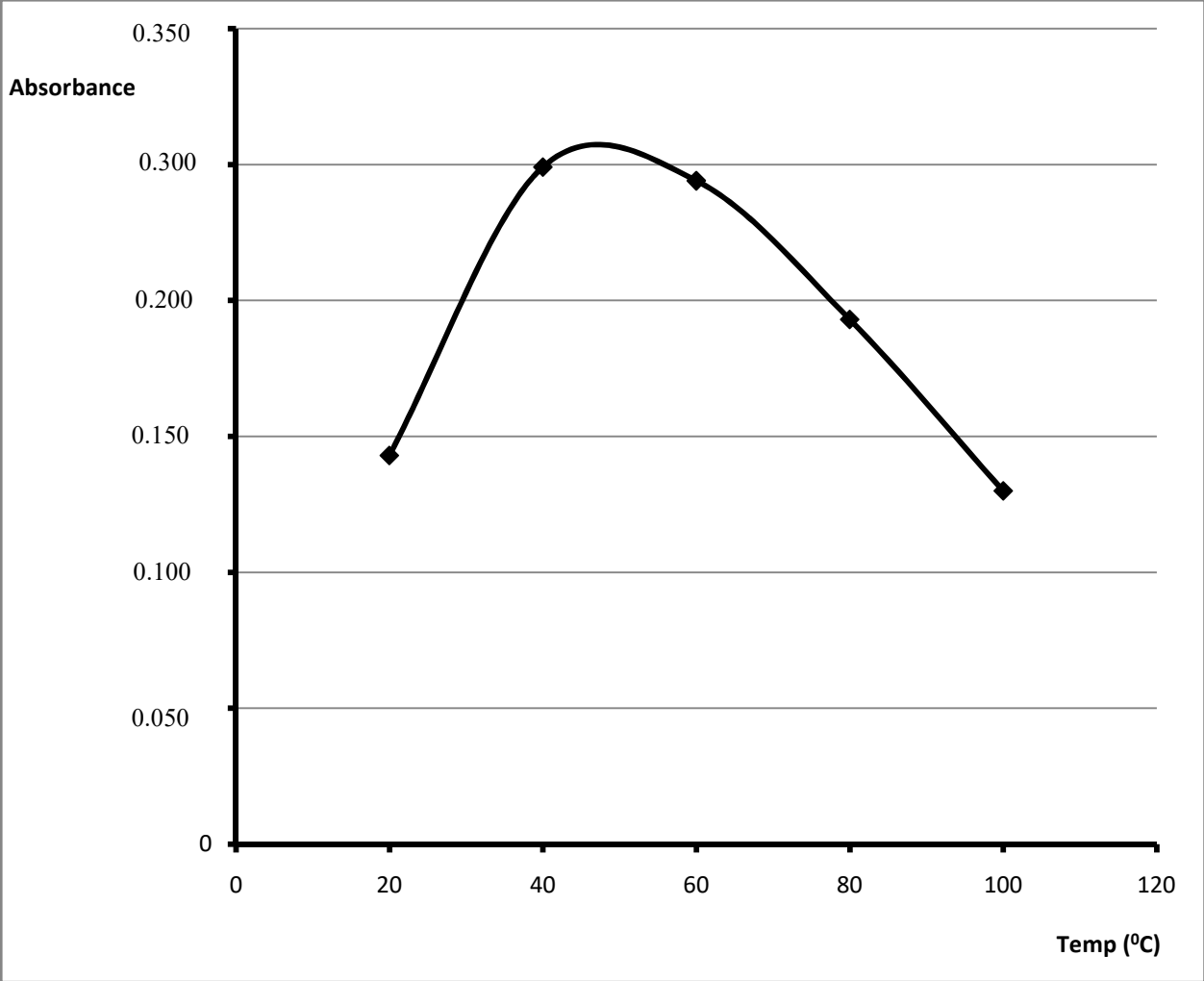


Fig. 4.15: Absorbance of extracted dye concentrations from *Nesorgodonia papaverifera* at different temperature using water as solvent.

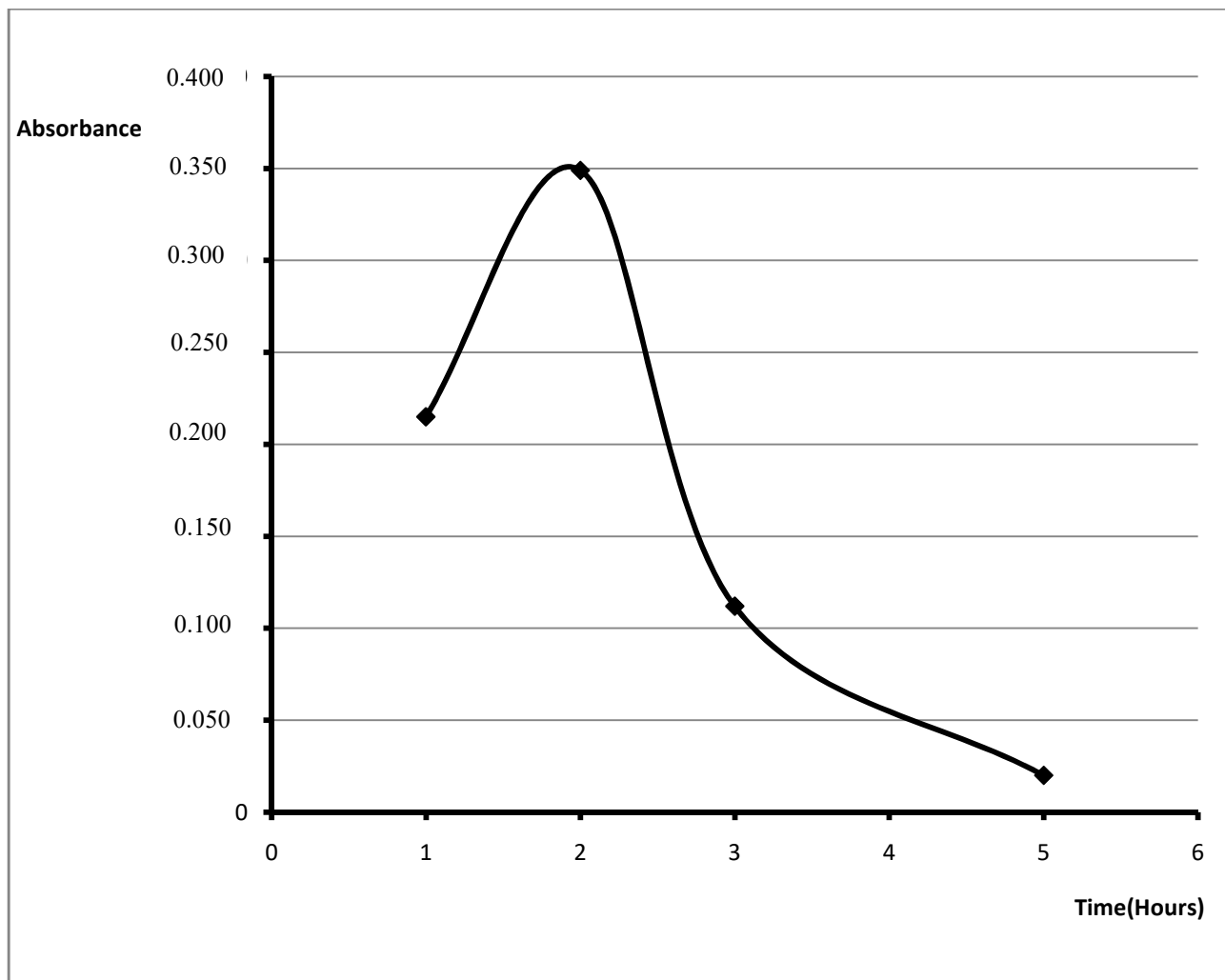


Fig. 4.16: Absorbance of extracted dye concentrations from *Nesorgodonia papaverifera* at constant temperature of 70 °C using water as solvent at different times in hours.

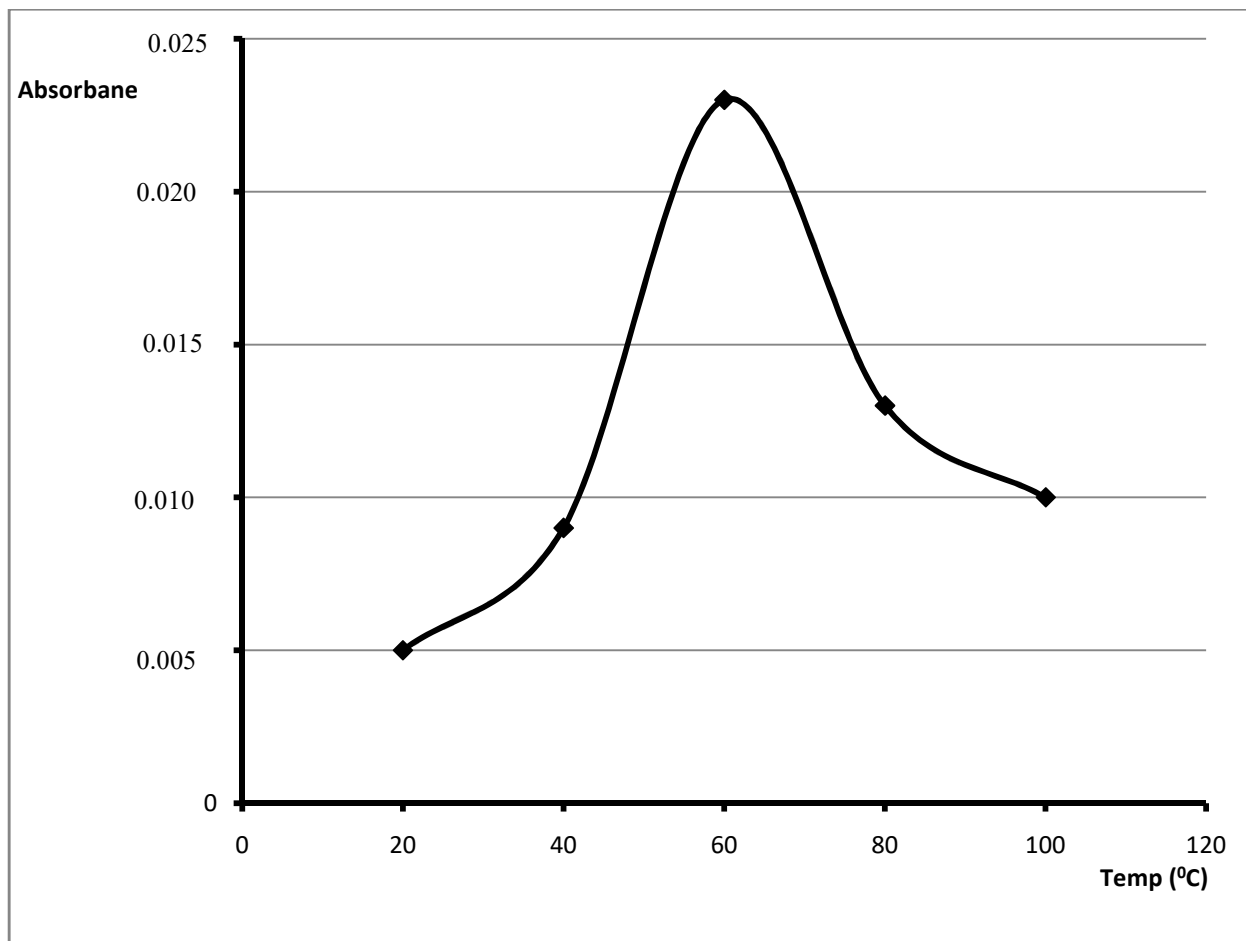


Fig. 4.17: Absorbance of extracted dye concentrations from *Nesorgodonia papaverifera* at different temperature using mixture of KOH and methanol as solvent.

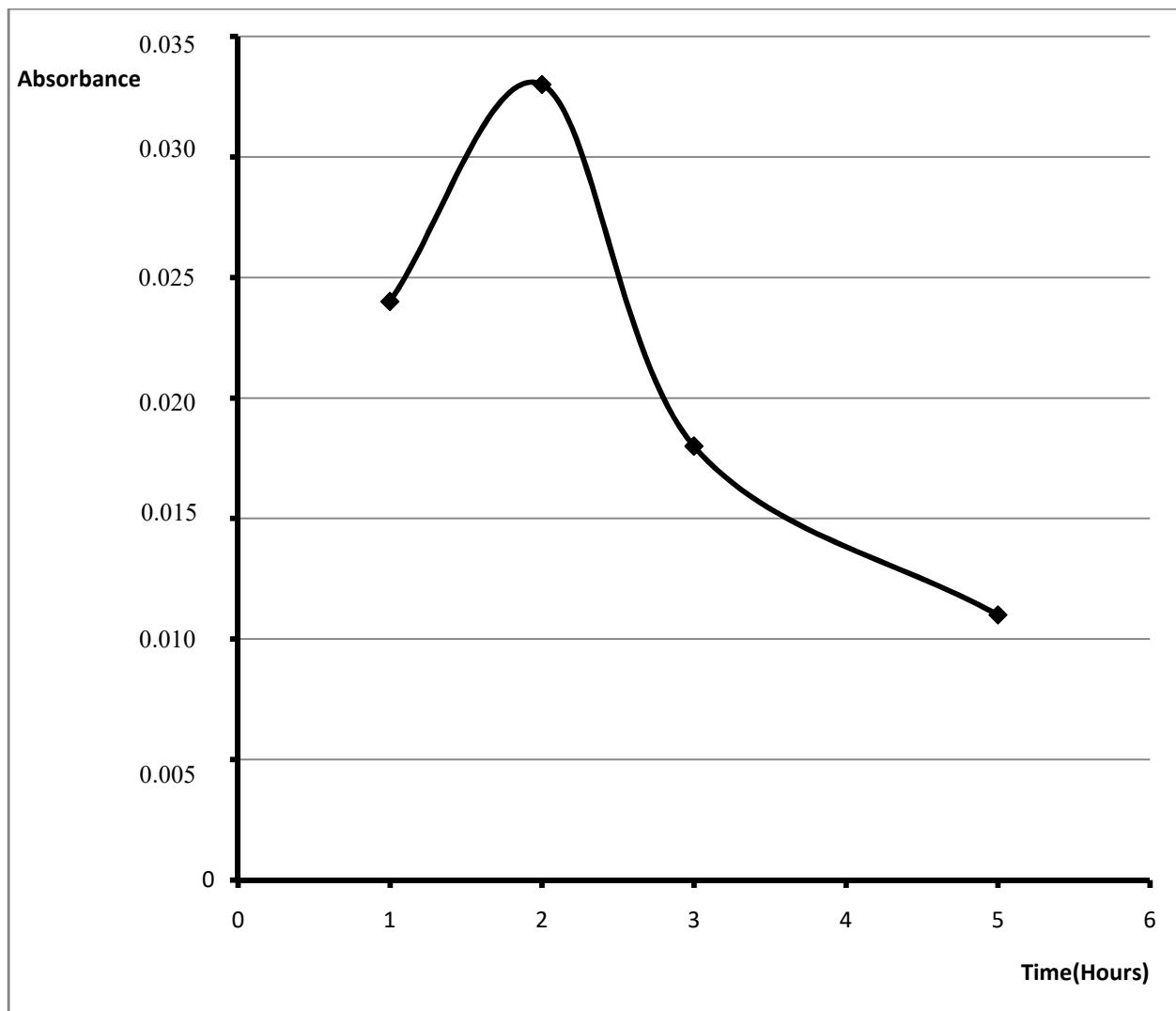


Fig 4.18: Absorbance of extracted dye concentrations from *Nesorgodonia papaverifera* at constant temperature of 70 °C using mixture of KOH and methanol as solvent at different times in hour.

Table 4.1: Spectral Data of dye extract from *Nesorgodonia papaverifera*

| | |
|------------------------------|--|
| FT-IR (KBr) cm^{-1} | 3596.4(OH), 2962(CH ₃), 2528.76(SH), 2324.3(C≡C), 2130.45(C≡C), 1924.06(AlkC≡C), 1649.19(C=O), 1413.87(C=C), 1280.78(Ar-CN), 1059.92(C-O), 873.78(C-C), 731.05(C-C), 418.57(C-Cl) |
| ¹ H NMR | 1.546-1.669(3H, CH ₃), 3.991-3.998(3H, OCH ₃), 4.607(1H, CH), 5.243-5.924(1H, OH). |
| ¹³ C NMR | 17.9(CH ₃ -C), 29.1(CH ₃), 29.3(CH ₂), 29.5(CH ₂), 29.7(CH ₂), 29.9(CH ₂), 54.2(OCH ₃), 57.2(CH), 207 (C=O) |
| Mass Spectrometrym/z (%) | 103(1.21), 107(2.25), 111(2.20), 111(2.58), 112(1.56), 112(42.32), 115(4.37), 129(15.25), 185(1.12), 264(2.14), 279(5.69), 284(10.83), 430(8.48) |
| UV-Visible | λ_{max} : 304nm and 748nm. Chromophores: C=O and -(C=C) ₅ - respectively |

Table 4.2: Spectral Data of dye extract from *Berlinia grandiflora*

| | |
|------------------------------|---|
| FT-IR (KBr) cm^{-1} | 3444.02(OH), 2955.04(alkyl CH ₃), 2346.48(C≡C), 2125.63(C≡C), 1647.26(C=O), 1401.33(C=C), 1057.03(C-O), 546.84(C-O-R), 392.53(R-O-R). |
| ¹ H NMR | 1.277 – 1.377(3H, CH ₃), 3.727 – 3.772 (3H, OCH ₃), 5.689-5.721(IH, OH) |
| ¹³ C NMR | 18.1(CH ₃), 29.1(CH ₂), 29.3(CH ₂), 29.5(CH ₂), 29.7(CH ₂), 29.8(CH ₂), 54.3(OCH ₃), 57.3(CH), 208.0(C=O) |
| Mass Spectrometrym/z (%) | 95(8.44), 103(0.53), 110(1.12), 112(15.11), 122(2.73), 125(0.74), 126(2.62), 139(1.44), 163(5.65), 178(1.00), 178(2.76), 178(4.67), 178(5.39), 178(6.29), 205(3.86), 218(1.45), 218(2.43), 218(2.70), 218(4.87), 224(2.26), 234(1.85), 236(1.80), 253(2.62), 256(5.87), 258(3.30), 260(4.11), 270(0.97), 284(342) |
| UV-Visible | λ_{max} : 371nm and 376nm Chromophores: =C-C=C-C=O and -C=C- respectively |

Table 4.3: Wash Fastness Properties of dye extract from *Nesorgodonia papaverifera* on cotton and nylon fabrics

| Fabric Type | Change in Colour | | | Staining of Adjacent White Fabric | | |
|-------------|--------------------|-------------------|---|-----------------------------------|-------------------|---|
| | Unmordanted Sample | SnCl ₂ | K ₂ Cr ₂ O ₇ | Unmordanted Sample | SnCl ₂ | K ₂ Cr ₂ O ₇ |
| Cotton | 2-3 | 4 | 4-5 | 3-4 | 4-5 | 5 |
| Nylon | 2 | 3-4 | 4 | 3-4 | 4-5 | 4-5 |

Wash Fastness: 1 – very poor; 2 – poor; 3 – fair; 4 – good; 5 – excellent.

Staining of Adjacent White Fabric: 1 – Deep staining; 2 – significant staining; 3 – moderate staining; 4 – very light staining; 5 – no staining.

Table 4.4: Wash Fastness Properties of dye extract from *Berlinia grandiflora* on cotton and nylon fabrics.

| Fabric Type | Change in Colour | | | Staining of Adjacent White Fabric | | |
|-------------|--------------------|-------------------|---|-----------------------------------|-------------------|---|
| | Unmordanted Sample | SnCl ₂ | K ₂ Cr ₂ O ₇ | Unmordanted sample | SnCl ₂ | K ₂ Cr ₂ O ₇ |
| Cotton | 2-3 | 4 | 5 | 3-4 | 4-5 | 5 |
| Nylon | 3 | 4 | 4-5 | 3-4 | 5 | 4-5 |

Wash Fastness: 1 – very poor; 2 – poor; 3 – fair; 4 – good; 5 – excellent.

Staining of Adjacent White Fabric: 1 – Deep staining; 2 – significant staining; 3 – moderate staining; 4 – very light staining; 5 – no staining.

Table 4.5: Light Fastness properties of dye extract from *Nesorgodonia papaverifera* on cotton and nylon fabric

| Fabric Type | Light fastness | | |
|-------------|-----------------------|-------------------|---|
| | Unmordanted Sample | SnCl ₂ | K ₂ Cr ₂ O ₇ |
| Cotton | 3 | 5 | 5 |
| Nylon | 3-4 | 4-5 | 5 |

1 – very poor; 2 – poor; 3 – fair; 4 – moderate; 5 – good; 6 – very good; 7 – excellent; 8 – outstanding.

Table 4.6: Light Fastness properties of dye extract from *Berlinia grandiflora* on cotton and nylon fabrics

| Fabric Type | Light Fastness | | |
|-------------|-----------------------|-------------------|---|
| | Unmordanted Sample | SnCl ₂ | K ₂ Cr ₂ O ₇ |
| Cotton | 3 | 3-4 | 5 |
| Nylon | 3 | 3-4 | 4 |

1 – very poor; 2 – poor; 3 – fair; 4 – moderate; 5 – good; 6 – very good; 7 – excellent; 8 – outstanding

Table 4.7: Rubbing Fastness properties of *Nesorgodonia papaverifera* dye extract on cotton and nylon fabrics

| Fabric Type | Rubbing Fastness | | | | | |
|-------------|--------------------|-----|-------------------|-----|---|-----|
| | Unmordanted Sample | | SnCl ₂ | | K ₂ Cr ₂ O ₇ | |
| | Dry | Wet | Dry | Wet | Dry | Wet |
| Cotton | 3-4 | 3 | 5 | 3 | 4-5 | 3 |
| Nylon | 3-4 | 3-4 | 5 | 4-5 | 5 | 3-4 |

Rubbing Fastness: 1 – very poor; 2 – poor; 3 – fair; 4 – good; 5 – excellent.

Table 4.8: Rubbing Fastness properties of cotton and nylon dye samples with *Berlinia grandiflora* dye extract

| Fabric Type | Rubbing Fastness | | | | | |
|-------------|--------------------|-----|-------------------|-----|---|-----|
| | Unmordanted Sample | | SnCl ₂ | | K ₂ Cr ₂ O ₇ | |
| | Dry | Wet | Dry | Wet | Dry | Wet |
| Cotton | 3-4 | 3 | 4-5 | 4 | 5 | 4-5 |
| Nylon | 4 | 3-4 | 5 | 4-5 | 5 | 4-5 |

Rubbing Fastness: 1 – very poor; 2 – poor; 3 – fair; 4 – good; 5 – excellent.

Table 4.9: Maximum exhaustion of the dye extract from *Nesorgodonia papaverifera* on the dyed fabrics

| Fabric | Dye Exhaustion (%) |
|---|---------------------------|
| Cotton without mordant | 56 |
| Cotton mordanted with CuSO ₄ | 76 |
| Cotton mordanted with SnCl ₂ | 68 |
| Nylon without mordant | 46 |
| Nylon mordanted with CuSO | 60 |
| Nylon mordanted with SnCl ₂ | 58 |

Table 4.10: Maximum Exhaustion of dye extract from *Berlinia grandiflora* on the dyed fabrics.

| Fabric | Dye Exhaustion (%) |
|---|---------------------------|
| Cotton without mordant | 58 |
| Cotton mordanted with CuSO ₄ | 80 |
| Cotton mordanted with SnCl ₂ | 72 |
| Nylon without mordant | 51 |
| Nylon mordanted with CuSO | 68 |
| Nylon mordanted with SnCl ₂ | 63 |

4.2 Discussion

4.2.1 Extraction

The results of the extraction of natural dye from *Berlinia grandiflora* and *Nesorgodonia papaverifera* using different solvents are presented in Fig 4.1 to 4.18. It shows the relationship between absorbance, temperature changes and changes in extraction hour.

From all the solvents used for the extractions of dye extract from *Nesorgodonia papaverifera*, acetone at 70 °C for two hours fig. 4.12 was observed to be the best solvent because it has maximum absorption while water at 40 °C for an hour fig. 4.5 proves to be the best solvent for the extraction of Berlinia dye extract as a result of its high absorption.

4.3 Characterization

4.3.1 Characterization of Dye Extract from *Nesorgodonia papaverifera*

The FTIR spectrum of *Nesorgodonia papaverifera* showed a very broad band at 3596.4 cm⁻¹ due to the presence of O-H stretch vibrations. The band at 2962.76 cm⁻¹ is assigned to the C-H stretch of alkyl (CH₃) groups. In the spectrum of the dye extract, vibrations occurred at band 2528.7cm⁻¹ suggesting the presence of COOH group, a sharp band at 1649.19 cm⁻¹ is indicative of the presence of C=O stretching vibrations. The band at 1413.87cm⁻¹ is assigned to C=C stretching vibrations. The absorption band at 1280.76 cm⁻¹ is assigned to characteristics vinyl ether and the absorbance at 1059.92 cm⁻¹, assigned to C-O group which confirms the presence of OH. The stretching peaks at 731.05 cm⁻¹ and 418.57cm⁻¹ confirm the presence of ethene group.

The ¹H NMR spectrum of *Nesorgodonia papaverifera* showed signals as singlet at δ1.55-1.67 were due to the presence of CH₃ proton, and the singlets at δ3.99 which suggest the presence of OCH₃ protons, singlet at δ4.61 suggest the presence of CH protons and the singlet at δ5.24-5.92 is assigned to the presence of OH protons.

The ¹³C NMR spectrum of *Nesorgodonia papaverifera* dye extract showed the following chemical shift values at δ17.9 which is an indicative of presence of sp³ carbon, chemical shift values at 29.1, 29.3, 29.5, and 29.7 are due to the presence of sp² hybridized carbon attached to and close to electronegative atoms. The chemical shift values at δ 54.2 and 57.2 suggests the

presence of sp carbons. The chemical shift value at $\delta 207.0$ suggests the presence of carbonyl carbon.

The mass spectrum of the dye extract from *Nesorgodonia papaverifera* showed the following m/z(%): 103(1.21), 107(2.25), 111(2.20), 111(2.58), 112(1.56), 112(42.32), 115(4.37), 129(15.25), 185(1.12), 264(2.14), 279(5.69), 284(10.83), and 430(8.48).

The UV-visible spectrum of the dye extract gave wavelength maxima range between 207nm and 748nm. These transitions may be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. This indicates the presence of chromophores such as $-(C=C)_5-$ and $C=O$.

4.3.2 Characterization of dye extract from *Berlinia grandiflora*

The FTIR spectrum of *Berlinia grandiflora* bark dye extract showed a very broad band at 3444.02 cm^{-1} suggesting the presence of OH stretching vibrations. The peak at 2955 cm^{-1} is characteristic of C-H stretching vibrations of alkyl group. The strong absorption band at 1637.26 cm^{-1} suggest the presence of C=O stretching vibrations. The absence of absorption peaks at $2700 - 2800 \text{ cm}^{-1}$ region indicates that the compound is not an aldehyde. The absorption band at 1401 and 1058 cm^{-1} are suggestive of the presence of C-O stretch. The broad peak at 546 cm^{-1} and 392 cm^{-1} suggest the presence of presence of ethene group.

The ^1H NMR of *Berlinia grandiflora* showed signals as singlet at $\delta 1.28-1.38$ which suggest the presence of CH_3 protons. The singlets at $\delta 3.73$ and 3.77 which suggest the presence of OCH_3 protons and the singlets at $\delta 5.72$ is indicative of the presence of OH protons.

The ^{13}C NMR spectrum of *Berlinia grandiflora* showed the following chemical shift value at $\delta 18.1$, which suggest the presence of Sp^3 hybridized (CH_3) carbons. The signals at $\delta 29.1, 29.3, 29.5, 29.7,$ and 29.8 are characteristics of Sp^2 hybridized (CH_2) carbons. The absorptions at $\delta 54.3$ and 57.3 are suggestive of Sp hybridized (CH) carbons that are probably attached to electronegative atoms. A carbonyl carbon ($\text{C}=\text{O}$) was also found at $\delta 208.0$.

The mass spectrum of *Berlinia grandiflora* showed the following m/z (%): 95(8.44), 103(0.53), 110(1.12), 112(15.11), 122(2.73), 125(0.74), 126(2.62), 139(1.44), 163(5.65), 178(1.00), 178(2.76), 178 (4.67), 178(5.39), 178(6.29), 205(3.86), 218(1.45), 218(2.70), 218(4.87),

224(2.26) 234 (1.85), 236(1.80) 253 (2.62), 256 (5.87), 258(3.30), 260(4.11), 270(0.97), 284(3.42).

The UV-visible of *Berlinia grandiflora* appeared in the wavelength range of 371.50nm – 376.50nm. These transitions may be attributed to $n \rightarrow \pi^*$. This suggests that the chromophores such as $=C-C=C-C=O$ and $-C=C-$ maybe present. This indicates the presence of non spectral colours.

4.4 Fastness Properties

4.4.1 Wash Fastness properties of dye extract from *Nesorgodonia papaverifera* on cotton and nylon fabrics.

The results of wash Fastness properties of dye extract from *Nesorgodonia papaverifera* on cotton and nylon fabrics were presented in Table 4.3. The result showed that when cotton and nylon were dyed without mordant, a fastness grade of 2-3 was experienced which indicates poor to fair fastness. When the dye was applied to the fabrics using mordant ($SnCl_2$ and $K_2Cr_2O_7$), the fastness grade increased to range of 4-5 in cotton fabric and 3-4 in nylon fabric respectively. This indicates a fair to excellent grade of fastness.

The staining of the adjacent undyed fabrics are more when the fabrics samples are unmordanted but slightly when mordanted. This shows that more of the dye molecules are fixed on the fabrics by the metal mordants and so can only be slightly washed off.

4.4.2 Wash Fastness properties of dye extract from *Berlinia grandiflora* on cotton and nylon fabrics.

The results of the wash fastness properties of dye extract from *Berlinia grandiflora* on cotton and nylon fabrics were presented in Table 4.4. The result showed that when the fabrics were dyed without mordant, a fastness grade of 2-3 was experienced which indicates a poor to fair fastness. When the dye was applied to the fabrics using mordant ($SnCl_2$ and $K_2Cr_2O_7$) the fastness grade increases to a range of 4-5. This indicates good to excellent grade of fastness.

The staining of the adjacent undyed fabrics are more when the fabrics samples are unmordanted but slightly when mordanted. This shows that more of the dye molecules are fixed on the fabrics by the metal mordants and so can only be slightly washed off.

4.4.3 Light Fastness of dye extract from *Nesorgodonia papaverifera* on cotton and nylon fabrics

Table 4.5 shows the light fastness results of the dye extract from *Nesorgodonia papaverifera* on Cotton and Nylon fabrics. The results show that when the fabrics were dyed without a mordant a fastness grade of 3-4 was observed which indicates an appreciable and significant degree of fading. Hence the light fastness is fair or moderate. When mordants were used, the fastness grade increases to a range of 4-5 which indicates a moderate degree of fading. Hence the light fastness is said to be good.

4.4.4 Light Fastness of dye extract from *Berlinia grandiflora* on cotton and nylon fabrics

The result of light fastness of dye extract from *Berlinia* on cotton and nylon fabrics are presented in Table 4.6. The results show that when the fabrics were dyed without mordant, a fastness grade of 3 was obtained which indicated a significant fading. Hence, the light fastness is fair.

But the light fastness improved to grade 4 – 5 on the addition of mordants. Of the two mordants used in this study, potassium dichromate gave the best light fastness.

4.4.5 Rubbing Fastness properties of cotton and nylon dyed samples with *Nesorgodonia papaverifera* dye extract

The result of rubbing fastness properties of cotton and nylon dyed samples with *Nesorgodonia papaverifera* dye extract are presented in Table 4.7. The results show that when the fabrics were dyed without a mordant (both wet and dry condition), gave rise to a rubbing fastness grade of 3-4 which indicates fair to good fastness grade. But when mordants were used in the dyeing, a fastness grade of 3 – 4 and 4 – 5 was obtained which indicates good to excellent fastness grade.

4.4.6 Rubbing Fastness properties of cotton and nylon dyed samples with *Berlinia grandiflora* dye extract

The result of rubbing fastness properties of cotton and nylon dyed samples with *Berlinia grandiflora* dye extract are presented in Table 4.8. The results show that when the fabrics were dyed without mordant, (both wet and dry condition) gave rise to a rubbing fastness grade of 3-4 which indicates fair to good fastness grade. But when mordants were used the dyeing, a fastness grade of 3 – 4 and 4 – 5 was obtained which indicates good to excellent fastness grade.

4.4.7 Maximum Exhaustion of the dye extract from *Nesorgodonia papaverifera* on the dye fabrics

The results of maximum Exhaustion of the dye extract from *Nesorgodonia papaverifera* on the dye fabrics are presented in Table 4.9. The highest percentage of exhaustion is associated with cotton fabric mordanted with CuSO_4 while the least percentage of exhaustion is associated with cotton fabric without a mordant. This implies that highest percentage of exhaustion is always noticed with fabrics dyed with a mordant.

4.4.8 Maximum Exhaustion of the dye extract from *Berlinia grandiflora* on the dye fabrics

The results of Maximum Exhaustion of the dye extract from *Berlinia grandiflora* on the dye fabrics are presented in Table 4.10. The highest percentage of exhaustion is associated with cotton fabric mordanted with CuSO_4 while the least is associated with nylon fabric without a mordant. This implies that copper mordant is a better one among the two mordant used for the study.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Natural colourants were successfully extracted from the bark of *Nesorgodonia papaverifera* and *Berlinia grandiflora* using several solvents. Dye extract from the bark of *Berlinia grandiflora* was extracted most by water as a solvent. Acetone was the best solvent for the extraction of colourants from *Nesorgodonia papaverifera*. The dye extracts were applied on nylon and cotton fabrics with and without mordants. The results obtained in this study suggest that the natural dye extracted from both plants possess intrinsic affinity for both natural (cotton) and synthetic (nylon) fabrics. The observed potential affinity of the dye extracts for the textile substrates used for the study may be due to the presence of biomordants such as tannins. The results of the study show that the dye extracts imparted non-spectral colours (brown) on the textile substrates. However, the addition of mordants improved the fastness performance of the dye extract on the fabrics. Potassium dichromate was preferred as a potential mordant because of its ability to produce better light fastness on both fabrics.

The characterization of the dye extract also suggested the presence of OH, CH₃, CH₂, CH, OCH₃, and C=O functional groups in the dye components. The chromophores in the dye extracts are C=O and $-(C=C)_5-$ for *Nesorgodonia papaverifera* and $=C-C=C-C=O$ and $-C=C-$ for *Berlinia grandiflora*.

5.2 Research Finding

The major findings in this research is that the two plants used for the research *Berlinia grandiflora* and *Nesorgodonia papaverifera* contains colourants which has affinity for both natural and synthetic fibres.

5.3 Contribution to Knowledge

1. The study established that this is the first time that natural dye have been extracted from *Berlinia grandiflora* and *Nesorgodonia papaverifera*.

2. The study also established that the extracted dye can be used for both natural and synthetic fibres.

5.4 Recommendation

The benefits of studying plant dyes and their applications on fabrics will improve the socio-economic and aesthetic value in the economy. With respect to the result of the study, the anti-microbial activities of the dye extract is recommended for further consideration.

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APPENDIX

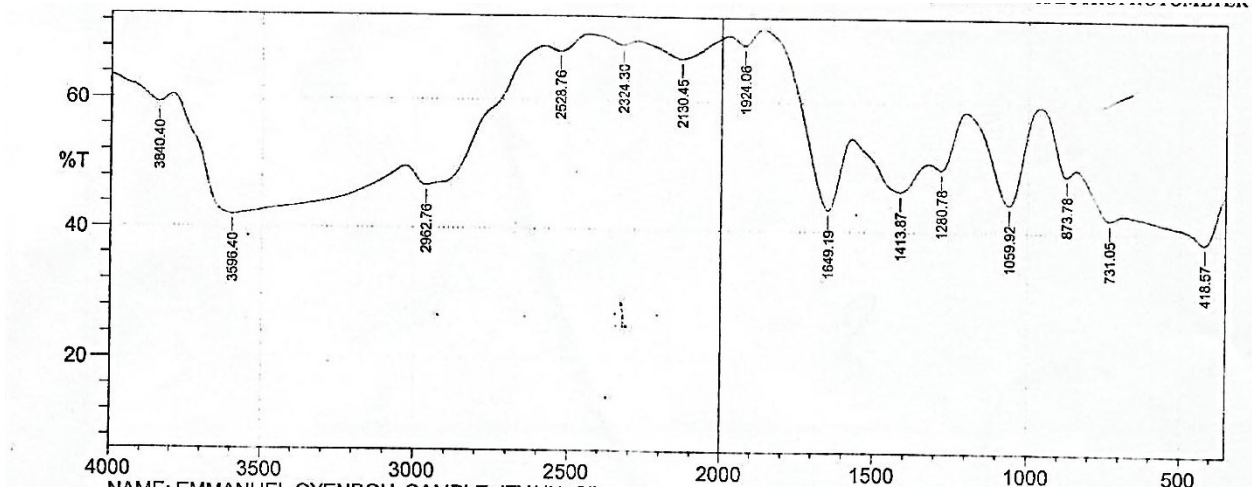


Fig. 4.19: FTIR Spectrum of *Nesorgodonia papaverifera* Extract

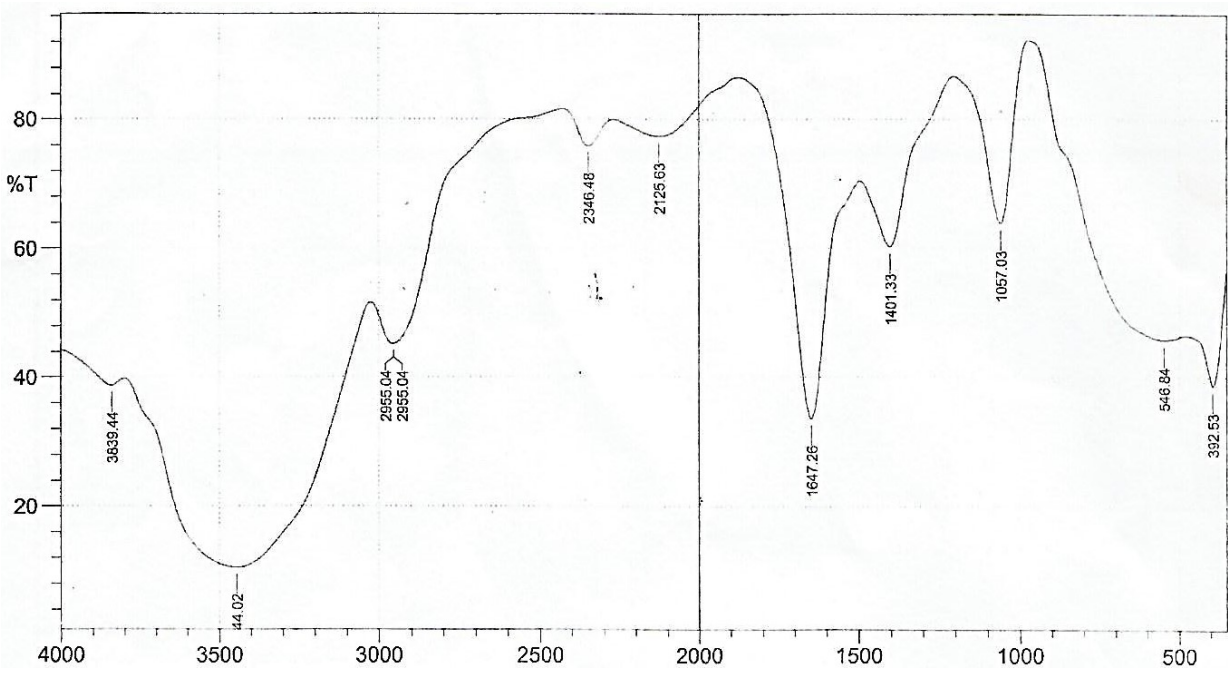


Fig. 4.20: FTIR Spectrum of *Berlinia grandiflora* Extract

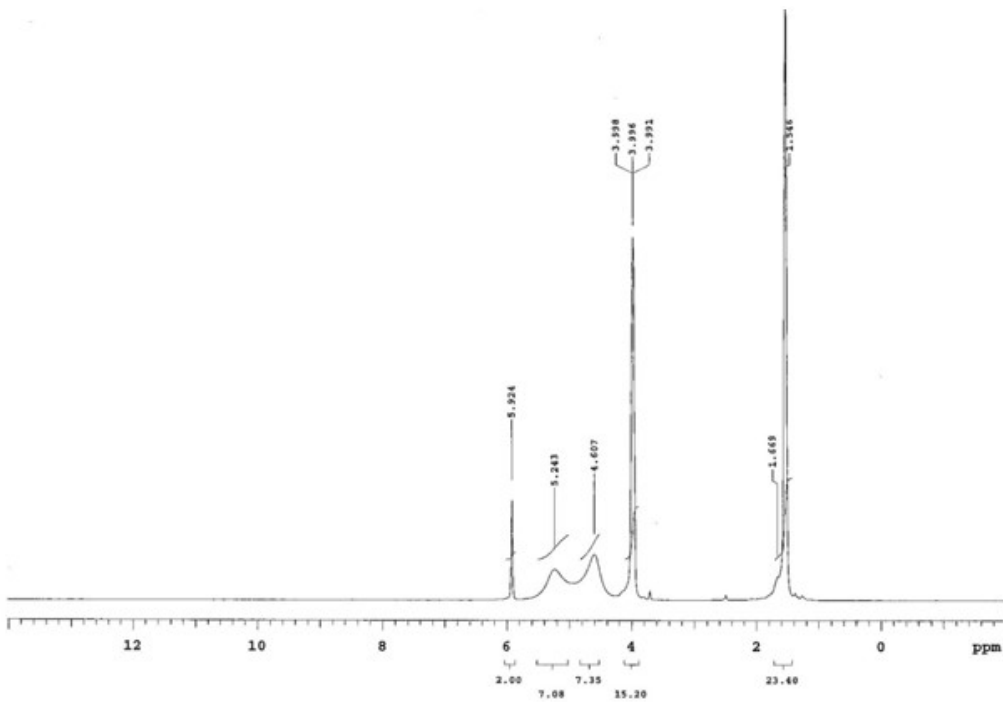


Fig. 4.21: ¹H MNR Spectrum of *Nesorgodonia papaverifera* Extract

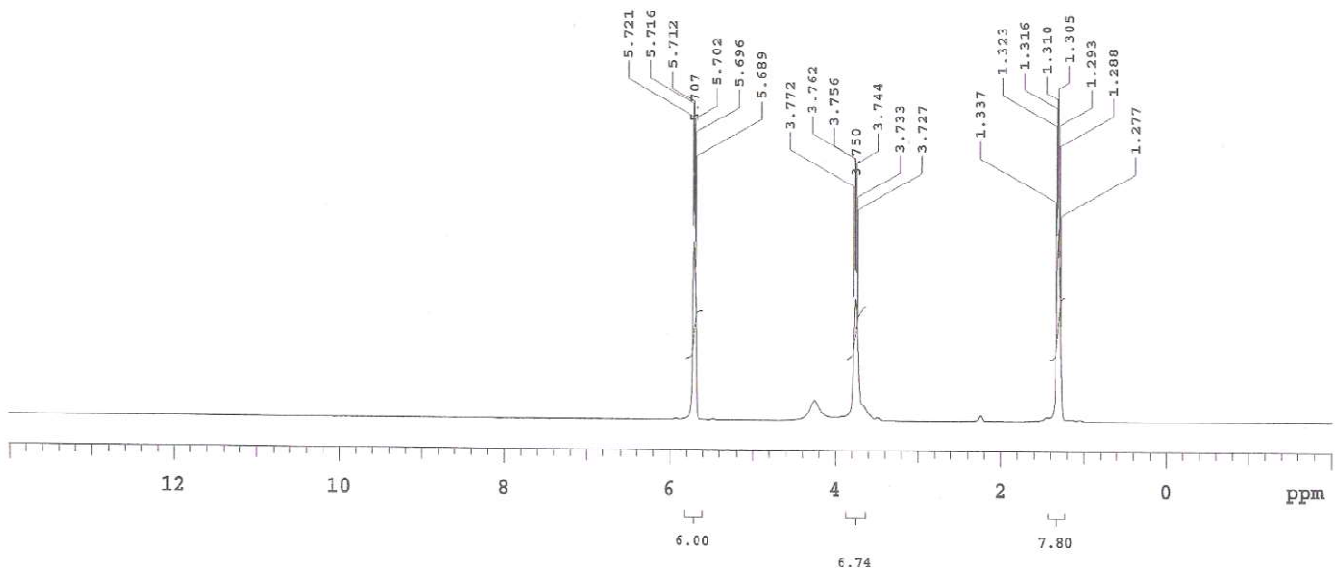


Fig. 4.22: ¹H MNR Spectrum of Berlinia Extract

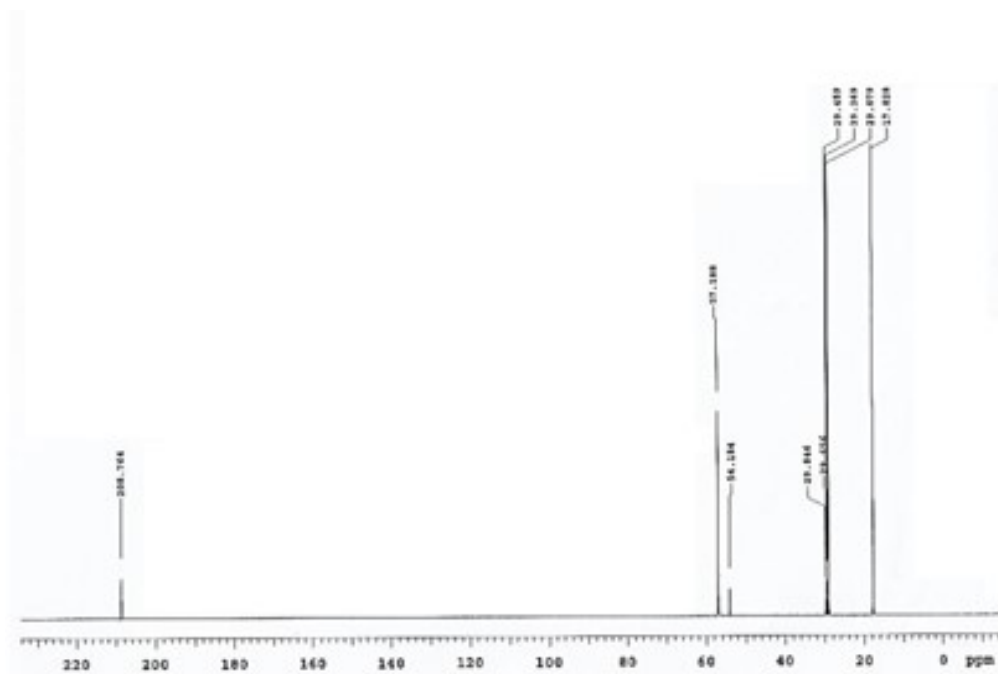


Fig. 4.23: ¹³C NMR Spectrum of *Nesorgodonia papaverifera* Extract

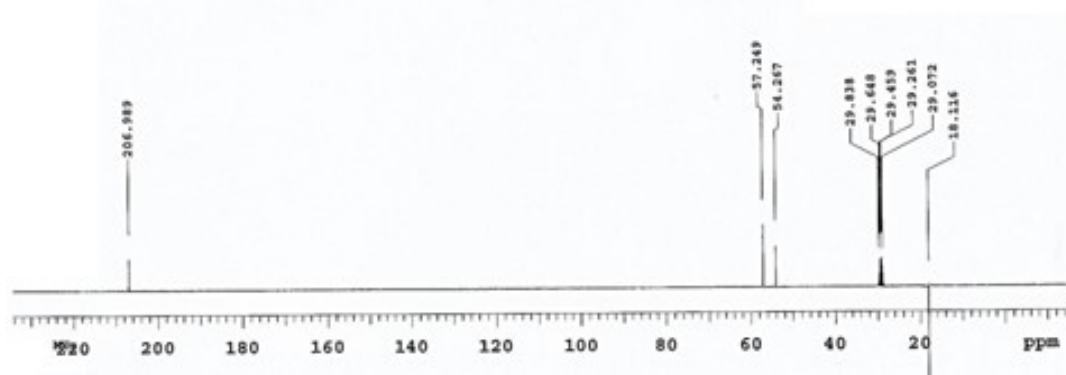


Fig. 4.24: ¹³C NMR Spectrum of *Berlinigandiflora* Extract.

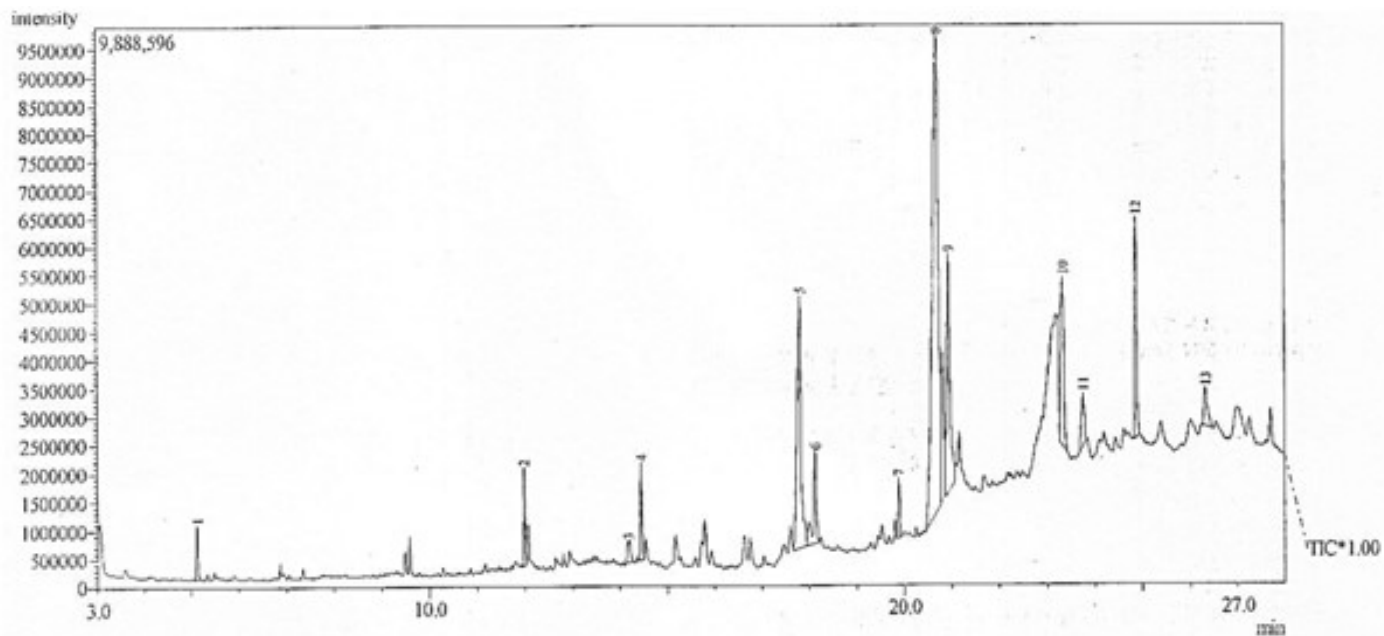


Fig. 4.25: GCMS Chromatogram of *Nesorgodonia papaverifera* Extract.

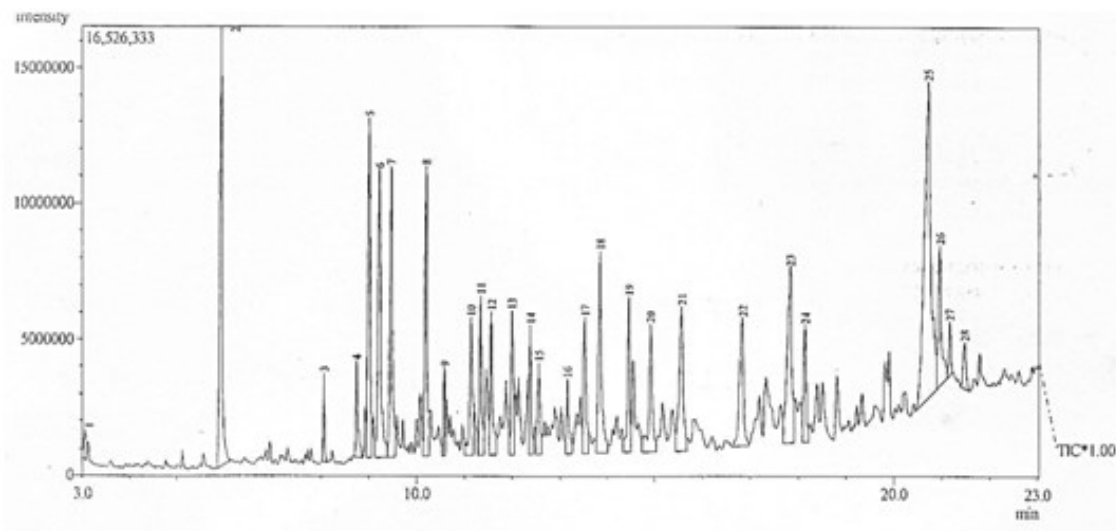


Fig. 4.26: GCMS Chromatogram of *Berlinigrandiflora* Extract

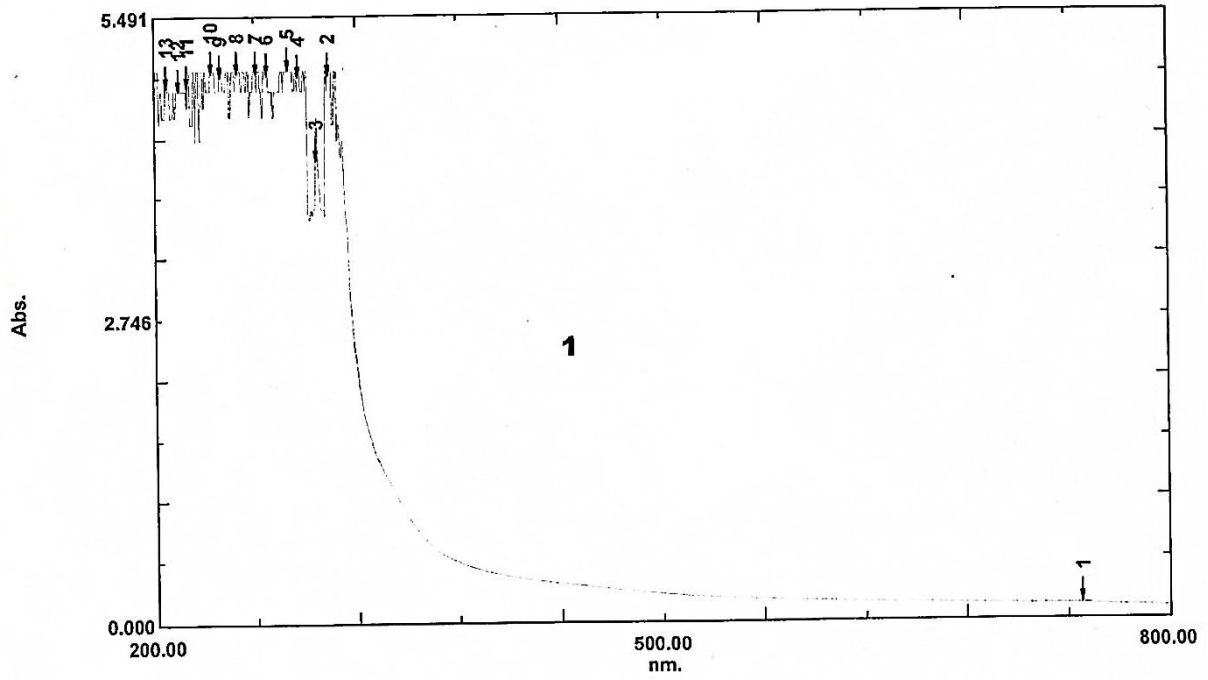


Fig. 4.27: UV-Visible Spectrum of *Nesorgodonia papaverifera* Extract

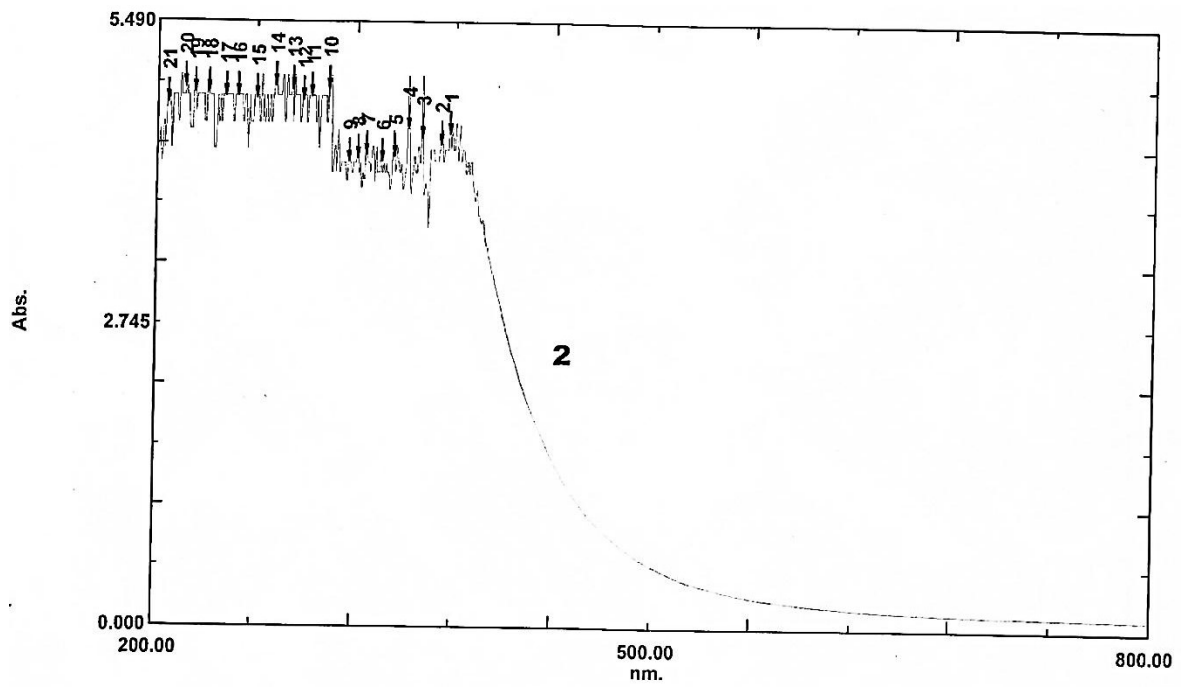


Fig. 4.28: UV-Visible Spectrum of *Berlinigrandiflora* extract

Grey Scale used for Description of Normal Fastness Grade

| Fastness grade | Shade change of sample tested | Fastness | Staining of adjacent white sample |
|-----------------------|--------------------------------------|-----------------|--|
| Grade 5 | No change | Excellent | No staining |
| Grade 4 | Slight loss in depth | Good | Very slight staining |
| Grade 3 | Appreciable loss | Fair | Moderate staining |
| Grade 2 | Significant loss | Poor | Significant staining |
| Grade 1 | Great loss in depth | Very poor | Deep staining |

Grey Scale Used for Description of Light Fastness Grade

| Fastness grade | Degree of fading | Light fastness |
|-----------------------|-------------------------|-----------------------|
| Grade 8 | No fading | Out standing |
| Grade 7 | Very slight fading | Excellent |
| Grade 6 | Slight fading | Very good |
| Grade 5 | Moderate fading | Good |
| Grade 4 | Appreciable fading | Moderate |
| Grade 3 | Significant fading | Fair |
| Grade 2 | Extensive fading | Poor |
| Grade 1 | Very extensive fading | Very poor |