SYNTHESIS AND APPLICATION OF AZO-ANTHRAQUINONE DISPERSE DYES ON POLYLACTIDE FABRICS.

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BY

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DEPARTMENT OF TEXTILE SCIENCE AND TECHNOLOGY,
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NIGERIA.

APRIL, 2014

DECLARATION

I declare that the work in thisthesis entitled Synthesis and Application of Azo-Anthraquinone Disperse Dyes on Polylactide Fabricshas been carried out by me in the Department of Textile Science and Technology. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other institution.

Peter Kayode OKAH______________ ______________

Name of Student Signature Date

CERTIFICATION

Thisthesis entitled Synthesis and Application of Azo-Anthraquinone Disperse Dyes on Polylactide Fabrics by Kayode Peter OKAH meets the regulations governing the award of the degree of Master of Science in Colour Chemistry and Technology of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research thesis is dedicated to Almighty God the beginning and the end, to my late father Mr. Raphael Olorunmowaju Okah and to the Colour Chemists all over the world.

ACKNOWLEDGMENT

My profound gratitude goes to Almighty God for keeping me in good health and making it possible for me to complete this research work.

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ABSTRACT

The synthesis of some disperse dyes base on anthraquinone was achieved by coupling diazotised 1-aminoanthraquinone and tetrazotised 1,4-diaminoanthraquinone respectively with pyridone derivatives. The identity of the resultant dyes were investigated using UV-visiblespectrophotometry, Fourier Transform – Infra Red and the relative molecular mass of the intermediates were confirmed using mass spectrometry. The applications of these dyes to polylactide fabrics were also studied. The results obtained indicated that the monoazo dyes exhausted better than the disazo dyes on polylactide fabrics. The fastness properties to washing, perspiration, sublimation and light were observed to be good to very good for all the dyed polylactide fabrics.

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ABBREVIATIONS

BASFBadisch Aniline und Soda Fabrik

BCBefore Christ

DMFDimethylformamide

et al.et alia (= and others)

FTIRFourier Transform – Infra Red

gGram

GC-MS Gas Chromatograph/ Mass Spectroscopy

ICIImperial Chemical Industries plc

ISOInternational Organisation for Standardization

kg Kilogram

KpaKilopascal

mMeta

m/e Mass to charge ratio

mlsMillilitres

molMole

OWF On weight of fabric

oOrtho

pPara

PETPolyethyleneterephtalate

PHA Polyhydroxyalkanoate

PLAPolylactic acid

TgGlass transition temperature

TMTrademark

TmMeltingtemperature

UV Ultraviolet

CHAPTER ONE

1.0 INTRODUCTION

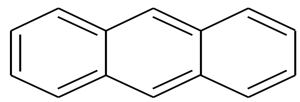
1.1 Dyes

A dye may be defined as a colorant that has substantivity for a substrate, either inherent or induced by reactants or more correctly, as a coloured substance capable of application in aqueous or non-aqueous solution or in an aqueous dispersion to a substrate so that the substrate acquires a coloured appearance. The substrate is usually textile fibre but may also be paper, leather, hair, fur, plastic material, food stuff or drug and so forth (Ogunmakin, 1992).

Dyes are coloured because they absorb light of a wavelength within the visible spectrum. This characteristic is promoted by the existence in the molecule of an organic compound of one or more certain unsaturated groups of atoms called “chromophores”. The most important of them are:

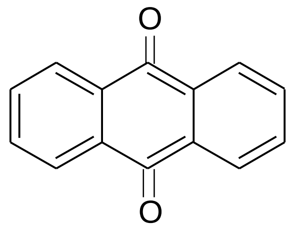
C=C	-	Ethylenic group
C=O	-	Keto group
-N=O	-	Nitroso group
-N=N-	-	Azo group
NO_2	-	Nitro group

When these chromophores are introduced into organic compounds that absorb light only in the ultraviolet region, these groups bring about absorption at lower frequencies and the new compound are coloured. For example, anthracene is colourless.



anthracene

But anthraquinone is a pale yellow compound, because it contains two keto groups C=O



Anthraquinone

In addition, certain substituents such as hydroxyl, amino and substituted amino groups greatly enhance the colour yielding properties of a chromophore but do not themselves result to absorption in the visible spectrum. These substituents are called auxochrome (Carr, 1995) and some are listed below:

NH_2	-	Amino
NH_2R	-	Alkyl amino (R = alkyl)
Cl, Br	-	Halogen groups
NHR_2	-	Di alkyl amino (R_2)
OH	-	Hydroxyl group
SO_3H	-	Sulphonic acid group
COOH	-	Carboxylic group

Unlike most organic compounds, dyes possess colour because they:

(1) absorb light in the visible spectrum (400–700 nm),

(2) have at least one chromophore (colour-bearing group),

(3) have a conjugated system, i.e. a structure with alternating double and single bonds,

(4) exhibit resonance of electrons, which is a stabilizing force in organic compounds (Abrahart, 1977).

When any one of these features is lacking from the molecular structure the colour is lost.

1.2 Pigment

This can be defined as a substance in a particulate form that is substantially insoluble in a medium, but which can be mechanically dispersed in this medium to modify its colour or light scattering properties or may be defined more correctly, as a natural or synthetic inorganic or organic substance that impacts a colour including black or white to other materials. Pigments may be in powder form or easily powdered substance mixed with a liquid in which it is relatively insoluble and used in making paints, enamels, and other coating material, inks, and rubber and also for imparting opacity and other desirable properties as well as colour. The main distinction between dye and a pigment is that, if the colorant has affinity for the substrate and will become a part of the coloured material without the need for an intermediate binder, it is considered a dye. This substantivity or affinity for the substrates clearly distinguishes dyes from pigments (Christie, 2001).

Pigment on the other hand must be incorporated into a binder to be attached to the substrate as in paint film attached to the wall of a house.

Dyes can be applied to textile fibre in two major ways, which are dyeing and printing:

Dyeing is a uniform application of colorant to textile substrates. Textile materials often show natural affinity for appropriate dyes and readily absorb them from aqueous solutions or dispersions giving the right pH, concentration and temperature with also the help of auxiliaries to control the rate of dyeing.

Textile printing involves the production of a predetermined coloured pattern on a fabric, usually with a definite repeat. It can be described as a localised form of dyeing, applying colorant to selected areas of the fabric to build up the design. Textile printing, like textile dyeing, is a process for applying colour to a substrate. However, instead of colouring the whole substrate (cloth, carpet or yarn) as in dyeing, print colour is applied only to defined areas to obtain the desired pattern. This involves different techniques and different machinery with respect to dyeing, but the physical and chemical processes that take place between the dye and the fibre are analogous to dyeing (Mazharul, 2011).

1.3 Fibre

Hearle (1963) quotes definition of a fibre according to the Textile Institute (1960) thus; a fibre is “a unit of matter characterized by fineness, flexibility, and high ratio of length to thickness” (Carr, 1995). There are many fibrous structures in nature, but only those which can be spun into yarns suitable for weaving or knitting are classified as textile fibres. For any fibre to have a commercial value, it must possess certain fundamental properties (Trotman, 1970). It must be readily obtained in adequate quantity at a price which will not make the end- product too costly. Such fibre must have sufficient strength, elasticity and spinning power. In addition to these fundamental properties there are others which are desirable, such as durability, softness, absence of undesirable colour, and affinity for dye.

In this work a new fibre known as Polylactide fibre is of great interest, its nature and dye ability with disperse dye is examined.

1.4 Polylactide Fibre

Recently substrates based on Polylactide (PLA) fibres have received attention worldwide because of their attractive advantages and their availability from a naturally renewable carbohydrate resource. In principle, PLA decomposes to carbon dioxide and water over time, without causing pollution to the environment. PLA can be conveniently produced from corn, sugar or sweet vegetables and is not a petroleum based material. At present, the proportion of corn crops used for PLA synthesis is less than 0.02% (Liang *et al*, 2010). This implies that the production of PLA cannot lead to potential food crisis.

PLA is an aliphatic polymer that is subject to high ultraviolet (UV) penetration into fabric composed of its fibres. Also dye performance is normally different on PLA as obtained in Polyethylene Terephthalate (PET). For instance, many commercial disperse dyes have exhaustion levels less than 50% on PLA but have exhaustion levels over 90% on PET (Liang *et al.*, 2010). Light fastness levels are also different on PLA and PET. Therefore, in addition to developing alternative dyeing methods for PLA, the synthesis of dyes that take the structural nature of PLA into consideration is essential to improving dye exhaustion and light fastness.

Petroleum-derived textile fibres accounted for 53.52% of the global textile fibre market in 2005.The production of these non-degradable and non-renewable synthetic polymers will definitely be affected by the crisis of oil depletion which is estimated to reach its peak production before 2025 (Mohammed *et al.*, 2011). The pollution resulting from millions of tons of packages incinerated every year, contributes to the global warming by greenhouse effect. These circumstances induced the need for new resources of degradable and renewable fibres which are more sustainable and environmentally friendly. A potential solution towards the environmental impact has been through the use of biodegradable polymers such as poly(lactic acid) $[(C_3H_4O_2)_n]$. These new biodegradable plastics have been used in various applications such as biomedical care products, packaging materials, and textile fibres. Sorona from DuPont, Polyhydroxyalkanoates (PHAs) and IngeoTM from Nature Works LLC are some examples of biodegradable polymers which have been successfully commercialized. IngeoTM are poly(lactic acid) fibres, which are the first biodegradable polymer made from 100% annually renewable natural resources, such as corn. PLA fibre such as Ingeo is very interesting fibre. It combines the performance of both natural and synthetic materials. Their properties like low inflammability, excellent UV stability, high resilience, excellent wicking, and moisture management are remarkable. However, the attractive biodegradability that gives PLA fibres their importance seems to be the weak point that prevents them from becoming more popular. Although PLA has great potential as substitute for Polyester (PET) fibre in cotton/polyester blends. They present different extents of degradation in an alkaline medium after cotton fabric preparation (Mohammed *et al.*, 2011).

Poly(lactic acid) as an aliphatic polyester, can be derived from 100% renewable resources such as corn. PLA, whose raw material (such as corn) is both renewable and non-polluting, eliminates the use of a finite supply of oil as a raw material. Poly(lactic acid) is the first melt-processable natural-based synthetic fibre, it is biodegradable, compostable and recyclable (Ozan, 2011) . Ease of melt processing, its unique property spectrum, renewable source origin, and ease of composting and recycling at the end of its useful life have led to a growing interest in PLA fibres and acceptance over a range of commercial textile sectors. PLA can be dyed with disperse dyes, just like PET fibres, under high temperature and pressure, although a modified dyeing method is employed since PLA has a low affinity to conventional water-soluble dyes. Conventional processes and finishing technologies can be used for processing PLA fabrics. The processing temperatures conventionally used for PET need to be reduced since the melting point of PLA is lower than that of PET. The PLA disperse dyeing conditions recommended by DyStar11 are 15–30 minutes at 110–115^{o}C at a pH of 4.5–5.0. As the dye bath is cooled down, disperse dye molecules are deposited on the surface of the fibres as relatively large particles due to their limited water solubility. These surface deposits of ‘unfixed’ dye can lead to a reduction in fastness properties as well as a dulling of the shade. Generally, a reductive clearing step is carried out after dyeing with disperse dye (Joonseok, 2011).

1.5 Azo Disperse Dyes

Disperse dyes are sparingly water soluble dyes. The most important class of disperse is the azo class. This class of azo disperse dyes may be further subdivided into four groups, the most numerous of which is the amino azo benzene class. This class can be altered to produce bathochromic shifts. A range of heterocyclic aminoazobenzene dyes are available. These give bright dyes, and are bathochromically shifted to give blues. The third class of disperse dye is based on heterocyclic coupling components, which produce bright yellow dyes under which this research work falls. The fourth class is disazo dyes. These tend to be quite simple in structure. Other than these, there are disperse dyes of the carbonyl class and a few from nitro and polymethine classes (Yusuf, 2012).

1.6 Justification

Dyes used on PLA fibres usually give low exhaustion and/or poor light fastness. It is hoped that synthesizing a low molecular weight dyes derived from pyridone as coupling component will provide good substantivity and better light fastness dyes for PLA.

1.7 Aim and Objectives of this Research

The aim of this research work is to synthesize some new azo dyes derived from anthraquinone as diazo component and pyridone as coupling component.

The specific objectives of this research work are:

i. To examine the effect of increasing alkyl chain length on pyridone
ii. To characterize the synthesized dyes.
iii. To apply the synthesized dyes on a non-woven Polylactide fabrics.
iv. To investigate the effect of variables such as temperature, time and pH on dye exhaustion on Polylactide fibre.
v. To investigate the performance properties such as wash, light and perspiration fastness.

1.8 Scope of this Work

This work is mainly to synthesize monoazo and disazo anthraquinone disperse dyes derived from pyridone as coupling component.

To compare the exhaustion of mono azo and disazo synthesized dyes.

To compare the fastness properties of these dyes on the Polylactide materials for example,, washing, light and perspiration.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Developments of Natural Dyes

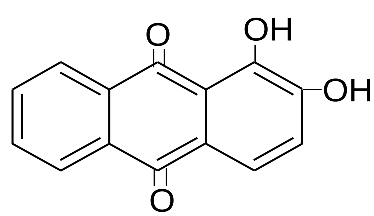
The technique of weaving was discovered in about 5000 BC (Katrina, 2013), it was inevitable that an attempt was made to colour the fabrics. The first natural dye to be discovered can only be a matter of speculation; however, it is highly probable that it was one of those occurring in brightly coloured flower which could be extracted by water alone to give a coloured solution from which the colour could be transferred to natural fibre directly by immersion. One common defect with the early natural dyes was their fugitiveness. Exposure to a few hours of bright sunlight would have faded the colour completely and washing would also remove all dyes. It is also believed that dyeing was practiced in China as early as 3000 BC (James, 2007). The earliest record of Indian religious social practices was about 250 BC and references were made to colour silk and gold brocades. As far back as 1450 BC, the ancient Egyptians were making textile material of astonishing delicate colour and were able to dye them in a whole range of colour. “Tyrian purple” the badge of Roman military was believed to have originated from the Phoenician city tyre (Heinrich, 2003).

2.1.1 Natural dyes

Until the middle of the last century, all dyes were derived from natural source. Indigo extracted from the plant *indigofera tinctoria,* and alizarin obtained from the root of the madder. All these natural dyes have been used in India since the beginning of recorded history. Equally too, our knowledge of Roman history informed us that "woad" was used by ancient Britons. This was obtained from the plant known as *isatis tinctoria* which was cultivated in Germany and in Britain (Heinrich, 2003). The active substance in the plant was indigotin, indigotin is blue but virtually insoluble in water, it must be reduced by fermentation by the ancient dyers before it was used. Tyrian purple has the same chemical structure as indigo, except that the two hydrogen atoms have been substituted by bromine. These two colouring matters belong to a group which is now known as the vat dyes. However, the following were the most important ancient natural dyes.

2.1.2 Alizarin

This was obtained from the roots of Rubia tinctorium, the active substance was madder when fermented yielded alizarin (Trotman, 1970).

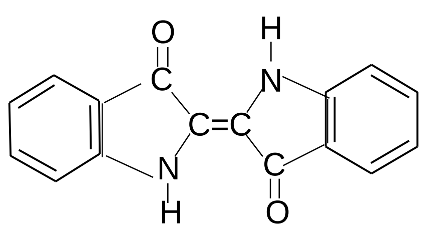


Alizarin

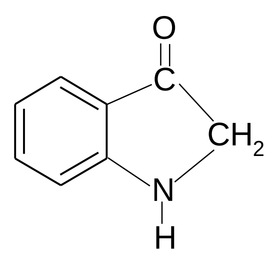
Cotton fabric was first immersed in a solution of alum followed by immersion in an extraction of wood ash; the fabric could then be dyed red colour by steeping it in a hot solution of alizarin. The effect of the treatment with alum followed by alkali was to deposit aluminium hydroxide in the fibre which when immersed in the dye bath combined with the dye to form an insoluble red lake. This pre-treatment is called mordanting and its discovery was very crucial to the development of natural dyes because of their lack of affinity for textile fibre (Belfer, 1972). Alum was the most important mordant throughout the era of natural dyes but other metals were also used to give different shades. Such metals were iron, copper salt, tin and chromium.

2.1.3 Indigo

Amongst the most ancient textiles ever discovered are those which have been dyed blue with indigo whose precursor is indoxyl.



Indigo

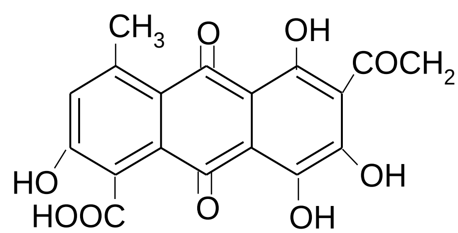


Indoxyl

There are two species of indigo, called *Isatis tinctoria* which grows in Europe and is commonly called woad by ancient Britons, and *Indigofera tinctoria*, which is indigenous to India, the parts of Asia and Africa, it is call “elu” in Yoruba land and were mostly used for dyeing ancient fabrics in blue colours. When the dead leaves of these plants ferment indicant is hydrolysed to indoxyl which is readily oxidized by air to indigo. The operation of reducing indigo in an alkaline was carried out in large vats and this method is termed vatting. Indigo dyeing originated from India.

2.1.4 Kermes

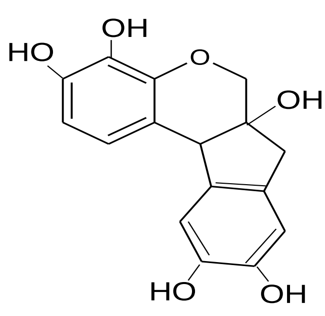
Kermes was another ancient dye which reference was made in the biblical account of the tabernacle curtains. The dyes were obtained from the dried bodies of the insect coccus ilicis found in the various species of oak trees growing in the Middle East. The colouring matter present was ‘kermesic acid’ which was originally applied on alum mordant (Mclaren, 1983).



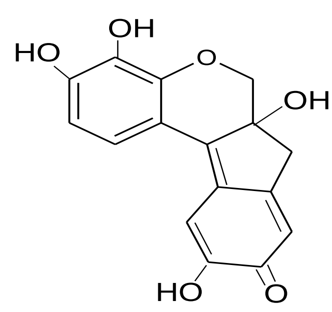
Kermesic acid

2.1.5 Log Wood

The ancient Mexican had been using a dye obtained from a tree growing on the shores of Campeche bay. The wood from this tree contained the colourless haemotoxylin which oxidized in air to red dye haematin. The shade it gave and the fastness properties depend on the mordant used (Jaime, 2003).



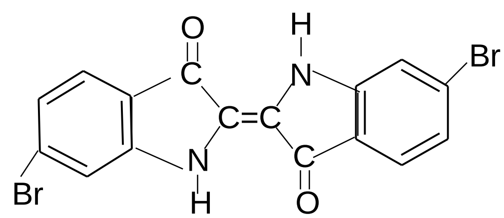
Haematoxylin



Haematin

2.1.6 Tyrian purple

This was discovered in about 1500 BC by the Phoenicians who were the most prestigious of all the dyers of antiquity (Belfer, 1972). The active colouring substance is derived from the secretion of molluscs known as murex and purpura. Different species of molluscs gave shade from reddish blue to reddish purple, the most beautiful shade being obtained by dyeing initially in a murex bath followed by a redyeing in a purpura bath. Friedlander in 1906 established the constitution of Tyrian purple to be 6,6-dibromoindigo (Ogunmakin, 1992).



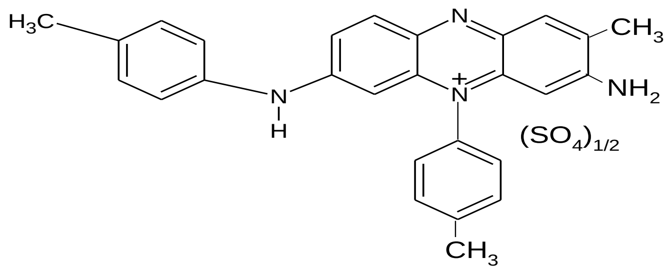
6,6-dibromoindigo

2.2 Developments of Synthetic Dyes

The year 1856 witnessed an event which was to bring about a fundamental change in the whole field of the chemical industry. Although the distinction of being the first synthetic organic dye belongs to picric acid which is the simplest dye known. Picric acid was a bright greenish yellow dye which belongs to the acid dye class (Garfield, 2001). But synthesis and manufacture of a purple dye by W.H. Perkins in 1856 is rightly regarded as the beginning of the synthetic dye era (Allen, 1971). In this year, William H. Perkins the son of builder was sent to the city of London school, where he showed aptitude for chemistry, which was under the guidance of Hoffman, the celebrated German chemist.

Perkins at the age of eighteen was attempting to synthesize anti malaria drug quinine by oxidizing aniline with acidified potassium dichromate. He obtained a black precipitate and observed that if these were extracted with naphtha and then with ethyl alcohol a brilliant purple solution was obtained. Further work on this experiment led him to conclude that they had produced useful dyestuff. Perkins work was of a profound significant because this was the first time a chemist had created a dye from simple organic molecules. More importantly, this product was made from what was virtually a waste product in the destructive distillation of coal in the gas works, and the discovery opened up an entirely new scene in the chemical industry.

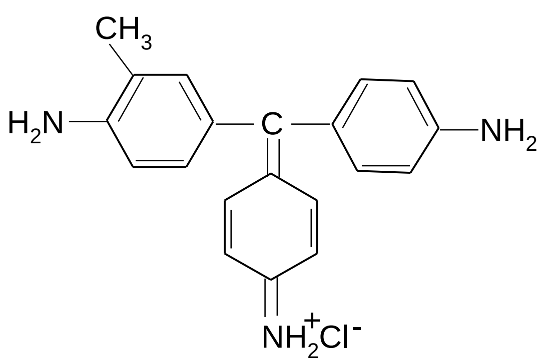
Perkins sent a sample of his dye to pillars' of Perth, who tried it out in their dyeing works and gave it a favourable report. Perkins therefore, at eighteen, assisted by his father and brother, built a factory at Greenford near London. He then devised and erected plant for benzene; he further pioneered the large scale reduction of nitrobenzene to aniline, and worked out a means of oxidizing the aniline and extracting the dyestuff (Gordon and Gregory, 1983). Aniline was a basic dye and Perkins had to develop methods of applying his products and demonstrate them to potential customers, thus starting the marketing concept of technical service which became a standard feature of all the dyestuff manufacturers in our modern age.



Mauveine

The birth of the synthetic organic dyestuff industry in 1856 was followed by a total dependence on coal tar as a source of aromatic for virtually the first 100 years. Since 1950s petroleum derived naphtha has taken over as the major source of monocyclic aromatics; coal tar however continues to be the major source of polycyclic aromatics (Gerald, 1988).

In 1858, verguin a French chemist, prepared magenta, another basic dye by heating impure aniline with stannic chloride to obtain a brilliant bluish red basic dye (Stork *et al.*, 2001).

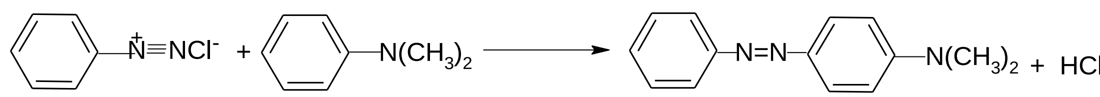


Magenta

Another important mile stone in the historical developments of synthetic dyes was in 1858 when Peter Griess, a German chemist in a Barton-on-Trent Brewery in Britain discovered the diazo reaction. He showed that when aromatic primary amines are treated with nitrous acid (produced by the action hydrochloric acid in sodium nitrite), they form diazonium salts as shown in this equation.

$$C_6H_5NH_2 + 2HCl + NaNO_2 \xrightarrow[< 5^{o}C]{} C_6H_5\overset{+}{N}\equiv NCl^- + NaCl + 2H_2O$$

The important properties of these compounds are that they will couple with aromatic amines and hydroxyl compounds to form highly coloured products which when rendered soluble by sulphonation produce a great range of dyestuffs known as azo dyes.



Diazonium compound   Dimethyl aniline   Dimethyl amino azobenzene

Some of the earliest dyes based on this reaction were Bismark brown by Martius in 1865 and Chrysoidine G was made in 1876 by Caro (Kent, 2007).

Another important land mark was the brilliant discernment of Kekule, a German chemist regarding the structure of benzene which led to a systematic study of the structures of aromatic hydrocarbons and their derivatives (Stork *et al*., 2001). In 1870, Kekule coupled diazotized aniline with phenol, and in addition, he made the first hydroxyl azo-dyes. He also determined the constitution of azo compounds. Prior to Kekule’s structural explanation of benzene, the early dyes discovered were purely based on empirical experiments and were all derivatives of benzene. Another important discovery in the synthetic of dyes which have profound influence on the dyestuff and related industries was the air oxidation of naphthalene to phthalic anhydride in the vapour phase using vanadium pentoxide as catalyst by Gibbs in 1927.

However, the following are brief comments of the historical developments of the major classes of dyes employed in the coloration of different types of textile fibres. Starting with basic dyes which were the first major synthetic dyes produced commercially.

2.2.1 Basic dyes

The beginning of the development of basic or cationic dyes goes back to the start of the chemical industry. Mauveine, a basic dye was the first to achieve commercial importance as earlier stated in this work. It was synthesized by an English chemist William Henry Perkins in 1856 (Christie, 2001). Other important basic dyes were fuchsine discovered by E. Nathanson in 1856. Magenta was discovered by a French chemist E. Verguin in 1859. Bismark brown by C. Martius in 1863. Crystal violet was also synthesized by Kern and Caro in 1882. Hoffman too, the celebrated German chemist, who was also the teacher of Perkins in England produces many dyes originally called Hoffman violets, some of which still survive till today were methyl violet and crystal violet the latter which was one of the medical dyes prescribed for healing wounds (Gordon and Gregory, 1983).

Henri Caro, a German industrial chemist was one of the greatest geniuses in early dye industry. Caro had little academic trading but learnt from his manufacturing experience, first with Roberts Dale and company in England and from 1868 with one of the first German dye makers, Badisch Aniline und Soda Fabrik (B. A. S. F.). Among his discoveries were alizarin, induling, eosine, Chrysoidine and methylene blue dyes and so forth (Beer 1959). So many are members of basic dyes which were synthesized by the inventiveness of the early dye chemists, all of which will be impossible to mention. Basic dyes are very brilliant and have intense tinctoral properties, their importance nowadays lie in their suitability for the dyeing of acrylic fibres.

2.2.2 Vat dyes (Indigoid)

Baeyer, a German chemist synthesized indigotin in 1880 and created a great scientific interest among the chemist working with B.A.S.F. to developed a technical synthesis in which phenyl glycine or its ortho-carboxylic acid was fused with caustic potash and it took a further seven years for the actual industrial production of indigo dyes (Gordon and Gregory, 1983). In 1899, Sandmeyer worked out synthesis of indigotin from aniline via isatin-anilide which also proved useful for the manufacture of indigoid and thio-indigoid dyes. Roessler showed in 1902 that indigoid could be obtained in good yield from phenyl glycine or its o-carboxylic acid if sodamide ($NaNH_2$) is used in the fusion. The dyeing of indigo was considerably simplified by the introduction of the hydrosulphide (dithionite) by Sohutzenberger a German chemist in 1871; this chemical has been serving a very useful purpose in textile chemistry since its discovery (Amstrong, 1950).

2.2.3 Anthraquinone vat dyes

Rene Bohn, a Swiss chemist working with the German firm of B.A.S.F in 1901 made an outstanding important discovery of indanthrene blue, a product of alkali fusion of β-amino-anthraquinone (Stork et al., 2001). He subsequently synthesized many other series of anthraquinone vat dyes, for example, indathrene yellow G or flavanthrone, indanthrene dark blue B or dibenzanthrone and so forth. The discovery of anthraquinone vat dyes was of very great commercial importance. Scientifically, the synthesis of Indanthrene blue stimulated intensive research on anthraquinone chemistry, which has resulted in the synthesis of a large number of complex ring system of both carboxylic and heterocyclic types involving novel condensations and new methods of cyclization. Davis, Fraser, Thomson and Thomas in 1920, methylated dihydroxydibenzanthrone to the dimethylether to synthesis Caledon Jade Green dye which is one of the most brilliant and fastest green dyes in the colour range of anthraquinone vat dyes (Aftalion, 1991).

2.2.4 Solubilised vat dyes

Bader and Sunder in 1924 prepared the first water soluble form of vat dyes as sulphuric esters of leuco derivatives, so that the vatting stage could be eliminated. Using an improved one stage method of reduction and sulphonation, ICI marketed Soledon dyes. Other commercial brand names in the series are indigosols and so forth. Vat dyes are mainly employed for the coloration of cellulosic fibres and its blends with synthetic fibres and have the highest fastness properties on cellulosic fibres among the cotton dyes (Aftalion, 1991).

2.2.5 Sulphur dyes

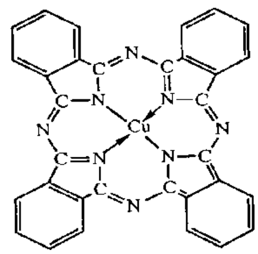
The first sulphur dyes were obtained in 1973 by Croissant and Bretonniere by heating organic cellulose containing wood saw dust, humus, bran, cotton waste and paper with alkali sulphide and polysulphides. The dark noxious smelling hygroscopic dyes obtained were soluble in water and produced greenish dyeing on cotton when applied from both alkali and alkali sulphide baths. On fixation by exposure to air or chemical oxidation with bichromate solution, the cotton became brown. These early sulphur dyes were sold under the trade name of Cachou de Laval. In 1893, sulphur dyes were first made from organic compounds of known constitution by Vidal, who found that various black dyes could be obtained by melting certain derivatives of benzene and naphthalene with sulphur and sodiumsulphide (Yanapati *et al* 1996). Sulphur dyes are mainly used for dyeing cellulosic fibres and blends of these fibres with synthetic fibres. Very little is known about the constitution of sulphur dyes in spite of their long history, consequently they are classified according to the chemical structure of the organic intermediates from which they are derived (Allen, 1971)

2.2.6 Direct dyes

Prior to 1884, all the synthetic dyes made had no affinity for cotton fibres. They could only be applied through mordanting, however, in 1884 Bottiger prepared Congo red (Kent, 2007). This dye could be applied simply to cellulosic materials from a hot bath with salt and was the first of the very many easily applied direct colours now available. Earlier in 1883, Walter had discovered sun yellow, a dye that has direct affinity for cellulosic fibres, but Bottiger’s dye is usually given pride of place. Direct dyes are mainly used for dyeing cellulosic fibres.

2.2.7 Phthalocyanine dye

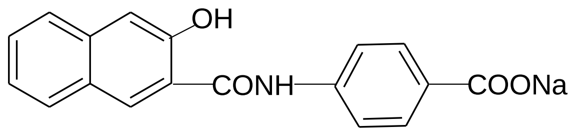
An event of great interest in the chemistry and technology of dyes was the manufacture of copper phthalocyanine, monastral fast blue BS in 1934 (ICI). The formation of a blue pigment during the manufacture of phthalimide in an iron pan was noticed by Dandridge in 1928 and the chemistry of phthalocyanines which are synthetic analogues of chlorophyll and hemin was elucidated by Linstead (Karlm *et al*, 2003). Copper phthalocyanine and its pentadecachloro derivatives are brilliant blue and green pigments of extreme stability. Phthalocyanine derivatives have been prepared which are useful for dyeing and printing textiles. Examples are Sirius light turquoise blue G (IG) and Alcian blue 8G ICI (1947), phthalogen blue IF3GM, IBM.



Phthalocyanine

2.2.8 Azoic dyes

An account of the discovery of the diazo reaction in 1858 by Peter Griess has earlier been made. In 1880, Read Holliday introduced the first insoluble azoic colour. It was made by padding cotton with an alkaline solution of beta-naphthol and later coupled with diazotized beta-naphthyl amine to give a colouring matter known as vacanceine red (Kent, 2007). Later, Meister, Lucius and Bruning extended the range. B. A. S. F. introduced para red, alpha-naphthyl amine bordeau and dianisidine. The year 1911 is notable for the discovery of naphtol AS by Zitscher and Lasca, this compound, the anilide of 2-hydroxy-3 naphthoic acid had a significant affinity for cellulose and was made by schopff in 1892, but the advantage as a coupling component were not realized then. This compound could be coupled with a variety of diazotized bases and was the forerunner of many analogous naphthoic acid derivatives (Trotman, 1970).



Naphtol AS

2.2.9 Acid dyes

Picric acid the simplest dye known and the first synthetic dye was an acid dye. The first commercial acid dye made was in 1862 by Nicholson, when he sulphonated aniline blue called Bleu de Lyons (Mclaren, 1983). Subsequently however, many basic dyes were converted to acid dyes by sulphonation making them more applicable to wool than basic dyes. The discovery of diazo reaction by Peter Griess in 1858 as earlier stated was quickly followed by the appearance of a very large number of acid dyes containing one or more azo groups. Ziegler in 1884 discovered pyrazolone azo dye known as tartrazine, which he obtained by heating phenyl hydrazine-p-sulphonic acid with dihydroxy tartaric acid. Acid dyes derived from anthraquinone started to appear in 1890. Another class of acid dyes is based on phthalocyanine structures. The trisulphonated derivatives of copper phthalocyanine, dyes wool in a very brilliant greenish blue shade (Karlm *et al*, 2003)).

2.2.10 Complex dyes acid mordant and metal

Mordant dyes operate on the simple principle that a number of metallic elements can act as acceptors to electron donors to form co-ordinate bonds. The earliest metal complex dyes were produced directly within the fibre by reacting a metallisable dye with a chromium compound in situ. The first chromium complex dyes prepared in substance, were the chromium complexes containing sulphonic groups, synthesized by Rene Bohn of B.A.S.F in 1912, these were known as ergan dyes (Peter and Anthony, 1992).The society for chemical industry in Basle, Switzerland, marketed the first neolan dye in 1915. The neolan dyes are preformed water soluble chromium complexes of mordant azo dyes which are applicable to wool and silk directly and eliminate the need for the dyer to carry out mordanting process.

2.2.11 Disperse dyes

The development of disperse dyes is inextricable linked with the development of synthetic fibres in 1938, DuPont de Nemours and co introduced the first synthetic fibre known as nylon. In 1959 E.I. DuPont commenced the commercial production of Orlon, and acrylic fibre. “Chemistrand in 1952 introduced acrilan, and courtelle was introduced into the market in 1957 by courtaulds”. Since then, the quantity of disperse dyes used for colouring the above named synthetic fibre have been very small and are only limited to pale shade because of technical limitations such as poor build up during dyeing, and poor fastness properties. However, the introduction of polyester fibre such as Terylene by ICI in 1948 and subsequently Dacron by DuPont proved to be a major land mark in the history of disperse dyes since they were the only classes of dyes to show reasonable substantivity for this fibre. The problems initially encountered in the coloration of polyester fibres were however overcome by the use of dyes of small molecular size followed by the use of carrier or accelerants at the boil (100^0C) and later the development of technical equipment of machine which allowed the use of temperatures typically 130^0C above atmospheric pressure which speeded up rate of dyeing to a commercially acceptable level. The theoretical aspects of disperse dye application have been investigated (Peter and Anthony, 1992). The application to cellulose acetate fibres was investigated by Kartaschoff and concluded that the insoluble disperse dye particles were attracted to the surface of the fibre from where they dissolved in the fibre to form a solid solution (Nkeonye, 1990). Vickerstaff and Waters obtained isotherm and concluded that the mechanism was of colloidal solution of the dye in fibre. Bird (1954) supported the theory first postulated by Clavel in 1924, that dyeing takes place from a dilute aqueous solution which is maintained in a saturated state by further dissolution of solid dye present in the dispersion. Giles has suggested that the solid solution condition is a special case of Langmuir adsorption. Peters in considering the thermodynamic of dye sorption also pointed out the similarities between solid solution and Langmuir adsorption. Today, there is a general acceptance of Clavel's theory that dyeing proceeds via aqueous solution to form a solid solution in the fibre.

Disperse dyes are traditionally non-ionic chemicals with sparing solubility in water which, consequently, are able to retain comparatively better substantivity for hydrophobic fibres, such as PET, PLA, nylon and acetate (Joonseok, 2011). For the sake of efficient diffusion into textiles, the particles of disperse dye should be as fine as possible comprising low molecular weight molecules in the range of 400 – 600. It is essential for disperse dyes to be able to withstand various dyeing conditions, pH and temperature, resulting in negligible changes in shade and fastness (Aspland, 1992). Disperse dyes are often substituted azo, anthraquinone or diphenylamine compounds which are non-ionic and contain no water solubilising groups. The dye particles are thus held in dispersion by the surface-active agent and the dyes themselves are called disperse dyes. They are marketed in the form of either an easily dispersible powder or a concentrated aqueous dispersion and are now the main class of dye for certain synthetic fibres (Ingamells, 1993).

2.2.12 Reactive dyes

Cross and Bevan in 1895 were the first to recognize the advantages to be gained by creating a chemical bond between a dye and a fibre. However in 1953, E.W. Stephen and I.D. Rattee of ICI achieved the Cross and Bevan reaction with cotton fibres under practical dye house conditions. “Stephen in his research work prepared some sulphonated azo dyes containing dichlorotriazinyl groups for wool dyeing” for Rattee to evaluate, but the dye sample failed to meet the wool dyeing target. However, the ICI chemists speculated that the chlorotriazinyl groups in the speculative dyes might be capable of reaction with alkali cellulose. Rattee confirmed this by first treating cotton in 15% solution of caustic soda and then immersing it in a cold solution of a dichloriazinyl dye and later rinsed the impregnated cotton materials he then realized that a dyeing of high washing fastness with no staining of adjacent undyed material was obtained (Peter and Anthony, 1992). Thus a new dye was created. Rattee and his colleagues therefore further concerned themselves with showing the existence of a covalent – dye – fibre – bonds and developing technically sound application techniques for evaluating further the speculated dyes.

2.3 Colour And Chemical Constitution

After Perkins’ synthesis of mauveine in 1857, little was known of the chemistry of dyes and the constitution of mauveine was not established until many years later. As more and more dyes were discovered and their properties studied, working rules emerged, whereby colour and dyeing properties could be related with structure.

Graebe and Liebermann (Ryes and Zollinger, 1972) in 1868 observed that all organic dyes then known were decolourised on reduction and they suggested that colour is associated with unsaturation. Witt (1976) in his own studies associated the colour of organic dyes to the presence of certain unsaturated groups of atoms which he called chromophores. Examples of such groups include the nitro ($-NO_2$), nitroso (-N=O), azo (-N=N-), ethylene (-CH=CH-) and carbonyl groups (-C=O). This however, is in good agreement with Graebe and Liebermann suggestion.

Witt (1976) ascribed the name chromogen to compounds containing such groups and showed that although they are coloured, they do not behave as dyes for fibres unless they are also substituted by basic or weakly acidic groups such as – NH_2, $-N(CH_3)_2$, or OH. The presence of these groups greatly increase the colour yielding power of a chromophore and for this reason they are called auxochromes. The presence of the auxochromes make the compound to have affinity for the substrate and also intensify the colour. Nietzki (1979) pointed out that the colour of dyes is deepened by the incorporation of substituents, the deepening effect being roughly proportional to the increase in molecular mass. Certain groups however, when incorporated produce hypsochromic effect (that is, shift of λmax to shorter wavelength) and serve as exception to this rule. Schultz (1892) examined Nietzki's rule in depth, pointing out many exceptions and in so doing coined the term bathochromic and hypsochromic shifts. These are now used to describe red (bathochromic) and blue (hypsochromic) shift in absorption spectroscopy.

The next major development was the quinonoid theory advanced by Amstrong (Amstrong, 1950). Amstrong pointed out that most dyes can be represented in a quinonoid form since quinines were known to be component of several colours. This is referred to as the quinonoid theory, however, Amstrong did not explain the reason why they gave rise to colour.

Baeyer in 1979 put further that colour might be due to "rhythmic" vibration which is caused as a result of oscillation of the quinonoid condition between two benzene rings (Griffiths, 1996). In the same year Hewitt and Mitchell observed that in azo dyes the depths of colour increases with the length of chain of alternating single and double bonds (conjugated chain) and ascribed this effect to the decrease in frequency of the chief oscillation (Siegfried, 1945). This was confirmed in quantitative experiments by Watson and Meek (Ryes and Zollinger, 1972). Watson in 1918 also pointed out that the depth of colour is affected by other factors beside the length of the conjugated chain because, if the dye molecule is weighted without altering the length of the conjugated chain, vibration become slower and the shade is rendered bluer. Thus on brominating fluorescein a deeper colour is obtained. This system was likened to a stretched string whose vibrations are slower by the increase in either its length or weight with the tension kept constant. The presence of an additional auxochrome as in polyhydroxyanthraquinone or the modification of an auxochrome as when an amino group is alkylated or arylated has also a marked deepening influence on hue (Watson and Edwin, 2013). Although, most dyes contain an auxochrome, the presence of such groups is not a pre-condition for dyeing ability because many dyes with one or more keto groups as chromophores have no auxochrome. However, on reduction to leuco form the vat dye possesses the hydroxyl group which functions as the auxochrome during dyeing. It is now usual to regard the molecule of a dye as consisting of a chromophoric system in which the classical chromophore forms part of a conjugated system of a single and double bonds often terminating in a polar atom or group which can exist in two adjacent states of covalency.

Bury in 1955 attributed the colour observed to the movement of electrons which give rise to two distinct but identical structures (Brooker, 1945). He described dyes as resonance hybrids of classical structures of similar stability but different charge distribution. With this theory, scientists began to consider colour and constitution from the standing point of the resonance theor**y.**

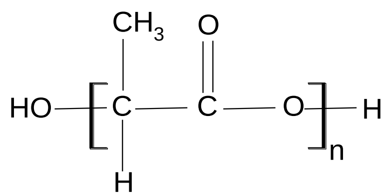
2.4 Poly(lactic) Acids

Poly(lactic) acid (PLA) is aliphatic polyester being considered as a green material due to its natural-based origin and biodegradability properties. Lactic acid obtained from the fermentation of sugar and vegetables for example, corn, and cassava is used as a monomer for PLA polymerization. Production of PLA polymer can be achieved by two major synthesis routes (Farrington et al, 2008), which are:

i) Direct condensation polymerization of lactic acid

ii) ring-opening polymerization of lactide.

Lactide is a cyclic dimer of lactic acid yielding poly(l-lactic acid), poly(d-lactic acid) or poly(l,d-lactic acid) depending on lactic acid isomers employed. The chemical structure of PLA is as shown.



Chemical structure of polylactic acid

PLA possesses desired properties required for packaging materials. Major market share of PLA therefore falls in the packaging industries. However its interesting properties have drawn attention from the textiles industry. An attempt to use PLA as a textile fibre has been pursued with the aim of replacing poly(ethylene terephthalate), PET fibre with this green polyester fibre. PLA fibre can be produced by both melt and solution spinning processes (Farrington *et al*, 2008) but the former is use more regularly due to the more eco-friendliness and ease of processing. Thermal degradation of the PLA polymer during melt spinning can be prevented by addition of a thermal stabilizer. The processing of PLA fibre/yarn is one of the important parameters in controlling the properties of PLA. PLA yarn which are formerly passed through different yarn processing possess different physical properties and morphological characteristics, which subsequently influence the accessibility of the chemical into the fibre during textile wet processing for example, dyeing and finishing (Jantip and Suwanruji, 2011).

2.4.1 Properties of polylactide fibres

PLA fibre has superior elastic recovery and a slightly higher hydrophilicity as compared with PET. It also exhibits lower flammability and less smoke generation. One of the important properties influencing dyeing properties of PLA is reported to be the effect of the lower refractive index. The refractive index of PLA was 1.45 while that of PET was found to be 1.58 (Vink et al., 2002). The lower refractive index of PLA causes a deeper shade of the disperse dyes obtained on PLA at the same applied dye concentration. The thermal properties of PLA were reported to be similar to that of polypropylene. The glass transition temperature Tg of PLA is 55-56^{o}C. The melting temperature (Tm) of PLA containing the L- or D-isomeric form alone is between 171-178^{o}C where as that of the stereocomplex analogue is 220^{o}C (Perepelkin, 2002). The most typically used PLA for textile application is poly(l-lactic acid). PLA has a lower melting temperature than PET. The melting temperature of PLA is at 170^{o}C while PET melts at 260^{o}C. This allows PLA to be processed at a lower temperature, for disperse dyeing on PLA is at 110^{o}C while PET is dyed at 130^{o}C (Suesat J, 2004). The heat setting of PLA is carried out at 130^{o}C whilst PET is heat set at 180^{o}c. These lower thermal properties are a cause of sensitivity of PLA fabric to high temperatures employed in textile processing and the conditions being experienced during its service life. Exposure to high temperatures could harm the fibre. Therefore, precaution is taken for the products obtained from PLA fibre to avoid ironing at high temperatures which can cause fibre damage. PLA is reported to be relatively sensitive to thermal degradation, especially at a temperature higher than 190^{o}C.

PLA is also sensitive to alkali. It can be destroyed more easily by alkaline hydrolyses than PET. Thus, it can be deteriorated by those using alkaline wet processing in textiles production. Under alkaline conditions, PLA can be damaged by an alkaline hydrolysis reaction. The fibre surface is eroded and its strength is impaired, especially at high temperatures. An example of the alkaline preparation process is peroxide-bleaching used to whiten the cotton component in the PLA/cotton blend. Therefore, the preparation, dyeing and finishing processes for PLA should be milder than those used for PET. It is suggested to process PLA fibre at lower alkalinity, processing temperature and time.

2.4.2 Dyeing PLA fibre with disperse dyes

Although PLA fibres exhibit many attributes similar to other synthetic fibres, they are a new category that requires modified dyeing and finishing techniques to maximize their benefits. The dyeing properties of PLA fibre has been intensively studied and owing to its relatively hydrophobic nature like PET, PLA fibre can be dyed with disperse dyes (Jantip and Suwanruji, 2011).

2.5 Heterocyclic Disperse Dyes

Effort by dye researchers to combine the brightness and fastness properties of anthraquinone dyes with strength and economy of azo dyes has yielded dividend with heterocyclic azo dyes which fall into two main groups: those derived from heterocyclic coupling components and those derived from heterocyclic diazo components. All the heterocyclic coupling components which provide commercially important azo dyes contain only nitrogen as the hetero atom. They are indoles, pyrazolones, and especially pyridones -

they provide yellow to orange dyes for various substrates (Yusuf, 2012). In contrast to the heterocyclic coupling component, all the heterocyclic diazo components that provide commercially important azo dyes contain sulphur either alone or in combination with nitrogen (El-Kashouti *et al.*, 2008).

2.6 Fibre Structure in Relation to Dyeing

Textile fibres, whether natural or synthetic consist of polymer molecules as their fundamental units. The functional groups within the polymers retain their chemical properties and determine the types of dyestuff for which the fibre have affinity for. In fact, fibres having many polar functional groups (hydrophilic fibres) will have greater affinity for the ionic dyestuff, while those having very low polar groups or nothing at all (hydrophobic fibres) will have greater affinity for non-ionic dyestuff. Crystallinity tends to impart hydrophobicity on fibres even when they have polar functional groups. This is due to the screening off of polar functional groups with possible intermolecular hydrogen onds. Also, the close arrangement of polymer molecules leaves little or no space for dye molecules to penetrate into it from the dyeing bath (Peter and Ingamells, 1973).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

The chemical used in this work were of analytical grade reagents. These are; ammonia water, methylamine, ethylamine, butylamine, dodecylamine, ethylacetoacetate, ethylcyanoacetate, sulphuric acid, sodium nitrite, tetrafluoroboric acid, 1-aminoanthraquinone, 1,4-diaminoanthraquinone, dimethylformamide, ethanol, sodium hydroxide, urea and distilled water. Polymeric materials used were 100% Polylactide non-woven fabric obtained from main store of the Department of Textile Science and Technology.

3.2 Apparatus and Equipment

Apparatus : Buckner flask, buckner funnel, 50ml beaker, 250ml beaker, reflux apparatus, magnetic stirrer, filter paper, thermometer, measuring cylinders, oven, heating mantle/plate, glass funnel, spatula, glass rods, watch glasses, electronic balance, 250ml volumetric flask, sample bottles, test-tubes, wash-bottle, pH-meter, Gallenkamp melting point apparatus, UV-visible spectrophotometer.

3.3 Methods

The methods adopted for this research work were of scientific approach, weighing and measuring all chemicals with adequate precautions. The results were recorded as quickly as possible to avoid human error.

3.4 Synthesis of the Intermediates

The intermediates were synthesis using three components only, these are; ethylacetoacetate, ethylcyanoacetate and the respective alkyl amine**.**

3.4.1 Synthesis of 1-amino-2-hydroxy-4-methyl-5-cyano-6-pyridone (4a)

A mixture of (0.1 mol, 11.3g) ethylcyanoacetate (28.2ml) and (0.3 mol, 10.5g) ammonia water (72 mls) were stirred until a clear solution was obtained and (0.1 mol, 13.0g) ethylacetoacetate (39.3 mls) was added. The mixture was refluxed at 110^{o}C for nine hours. During the process no moisture was allowed in or out of the refluxing set up unit. This was achieved by placing an L-shaped tube containing calcium chloride powder at the top outlet of the condenser. The L-shaped tube was blocked at the two ends using cotton wool. In the process white precipitate was obtained which was collected and washed with distilled water, dried in oven and recrystallized from ethanol.

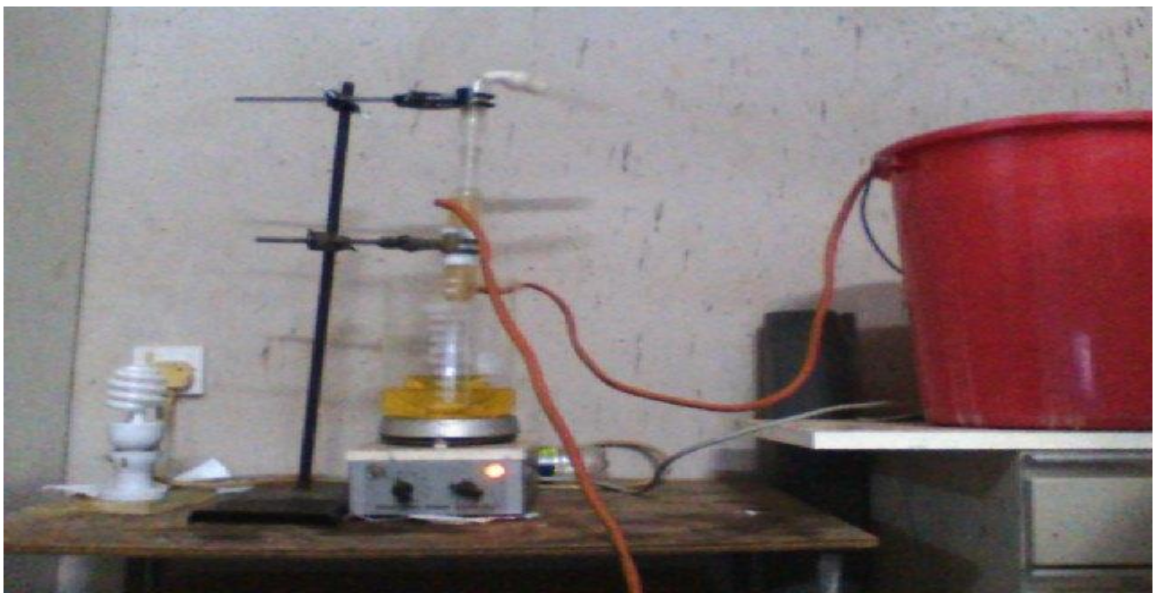


Plate 3.1: Set up for the synthesis of pyridone

3.4.2 Synthesis of 1-methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4b)

The above procedure was followed using methyl amine instead of ammonia water to produce dye intermediate 4b. After 9 hours of refluxing, the reaction mixture was poured in 400 ml of distilled water and was acidified with hydrochloric acid to obtain white precipitate which was washed, dried and recrystallized from ethanol.

3.4.3 Synthesis of 1-ethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4c)

The above procedure for 4b was followed using ethyl amine instead of methyl amine to produce dye intermediate 4c. Similarly after 9 hours of refluxing, the reaction mixture was poured in 400 ml of distilled water and was acidified with hydrochloric acid to obtain white precipitate which was washed, dried and recrystallized from ethanol.

3.4.4 Synthesis of 1-butyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4d)

The above procedure for 4c was followed using butyl amine instead of ethyl amine to produce dye intermediate 4d. Similarly after refluxing for 9 hours, the reaction mixture was poured in 400 ml of distilled water and was acidified by hydrochloric acid to obtain white precipitate which was washed, dried and recrystallized from ethanol.

3.4.5 Synthesis of 1-dedocyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4e)

The above procedure for 4d was followed using dodecyl amine instead of butyl amine to produce dye intermediate 4e. Similarly after refluxing for 9 hours, the reaction mixture was poured in 400 ml of distilled water and was acidified by hydrochloric acid to obtain white precipitate which was washed, dried and recrystallized from ethanol.

3.5 Diazotisation and Coupling

3.5.1 Diazotisation and Coupling Procedure for Synthesis of Dyes (7a, 7b, 7c, 7d and 7e).

The procedure used is illustrated for the synthesis of dye 7a. Sodium nitrite ($NaNO_2$) (0.015mol, 1.04g) in 5ml of water was added drop-wise to a solution of 1-aminoanthraquinone (0.01mol, 2.32g) dissolved in concentrated sulphuric acid (98% w/w, 20ml) with stirring at 5^oC . After 1hour, tetrafluoroboric acid (HBF_4) (4g, 40% w/w) was added as a precipitating agent at 5^oC and the mixture was stirred for another 30minutes.The diazonium salt (6) was isolated by filtration of the tetrafluoroborate salt which was then washed with 300ml of water. A solution of the diazonium compound in dimethylformamide (DMF) (30ml) was cooled to 5^oC and 1-amino-2-hydroxy-4-methyl-5-cyano-6-Pyridone (0.01mol, 1.5g) dissolved in 10 ml of 1M sodium hydroxide solution was added in four equal proportions at 3minutes interval. After stirring the mixture for 30 minutes at 5^oC, 250ml of water was added, filtered and washed with 300ml of water to obtain dye 7a. Following the above procedure, dyes **7a – 7e** were produced.

3.5.2 Synthesis of dyes 7f and 7g

Dyes 7f and 7g were produced by coupling diazonium salt with 1- naphthol and 2-naphthol respectively as coupling components.

3.5.3 Tetrazotisation and coupling procedure for the synthesis of dyes 10a,10b, 10c, 10d and 10e

Using the above procedure for diazotisation, 1, 4 – diaminoanthraquinone (8) was tetrazotised to obtain tetrazonium salt (9) which was then coupled with the synthesized pyridones (4a-4e) to produce disazo dyes (10a-10e).

3.5.4 Synthesis of dyes 10f and 10g

Dyes 10f and 10g were synthesized by coupling tetrazonium salt (9) with 1- naphthol and 2-naphthol respectively.

3.6 Purification of Dyes

The synthesized dyes were purified by recrystallization from ethanol. The structure, yields and melting points were determined and the results are shown in Table 4.1.

3.7 Percentage Yield of Dyes

The percentage yield of the synthesized dyes were determined using the formula shown below and the values are shown in Table 4.1

$$\%\,\text{Yield} = \frac{\text{MP}}{\text{MMP}} \div \frac{\text{MR}}{\text{MMR}} \times 100$$

Where:-

MP = mass of the product

MMP = molar mass of the product

MR = mass of the reactant

MMR = molar mass of the reactant.

3.8 Determination of Melting Point of the Dyes

The melting points were determined using the Gallenkamp melting point apparatus. Small sample of each of the synthesized dyes were placed in a capillary tube and then inserted into the melting point apparatus. The machine was put on and the temperature gradually increased to heat-up the sample in the capillary tube. The set up was monitored until the sample began to melt. The melting temperature was recorded and the procedure was repeated for other samples. The values obtained are shown in Table 4.1.

3.9 Infra-Red Spectral of the Dyes

The infra-red spectra of the dyes were determined using the FTIR spectrophotometer to determine the functional groups present. Also the structures of the intermediates were analysed using the GC-MASS spectrophotometer as shown in Figure 4.1 while the FTIR results are summarized in Table 4.2.

3.10 Visible Absorption Measurements

The wavelength of maximum absorption was determined for each dye in three solvents ethanol, ethanol plus hydrochloric acid, toluene and dimethylformamide (DMF). .001g were dissolved in 5mls of each of the above mentioned solvent. The spectra of the dyes solution were measured and recorded using UV–Visible spectral scan machine (Jenway 6405 uv/vis spectrophotometer) at Multi user laboratory, Chemistry department, Ahmadu Bello University, Zaria. The results obtained are as shown in Table 4.3.

3.11 Application of the Dyes on Polylactide Fabrics

Stock solution (1%) of each dye was prepared by dissolving 1g of the dye in 100mls of distilled water, a liquor ratio of 50:1was used, 2% shade o.w.f and 1.0g of Polylactide fabric.

The volume of the stock solution required was calculated using the formula (3.4)

$$V = \frac{P \ X \ W}{C} \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3.4)$$

Where:

P = percentage shade on weight of fabric

W = weight of fabric

C = percentage concentration of stock solution

3.11.1 Dyeing of the polylactide non-woven fabric

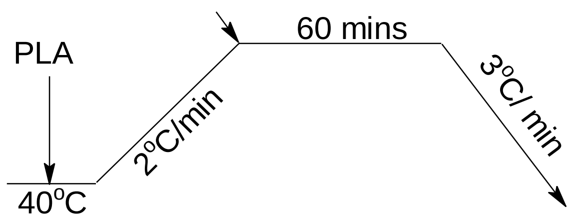


Figure 3.1: Dyeing profile of PLA with disperse dyes

The dye bath was prepared using a liquor ratio of 50:1; the volume of dye required was 2mls to give 2% depth of shade on weight of fabric measured in a beaker. For each respective dyeing, 1g of fabric was wetted in water for 5minutes and excess water squeezed out. The wetted fabric was then introduced into the dye solution on a regulatory steam bath with the dyeing liquor temperature at 40°C initially and raised to the boil after a period of 30 minutes while constantly agitating the sample. The dyeing was carried out at this temperature for 1 hour. After dyeing was completed, the fabric was removed, thoroughly rinsed with cold running water and dried at room temperature. The percentage exhaustion of the dyes was calculated using the striping method with DMF as the solvent.

Series of concentrations (range; 0.01-1.0g) of each synthesised dyes were dissolved in 20% DMF at the initial stage. The absorbances of each series were taken using UV-visible spectrophotometer. The absorbance values were plotted against concentration to obtain a calibration curve which gave a straight line in agreement with Beer-Lambert's law. Each dyed fabric about 1.0g was placed in a beaker and 20% of DMF in a liquor ratio of 50:1; this was stirred until almost all the dyes have been striped into the solution. Again the absorbances of the dye-striped solutions were measured with the UV-visible spectrophotometer. The corresponding concentrations of these absorbances were traced out from the calibration curve and each was expressed as a percentage of the dye-bath concentration. This is the percentage exhaustion of the dyes on the polylactide fibre. The results obtained for all dyes are shown in Figures 4.2 to 4.7.

3.11.2 Effect of temperature on dyeing

The dyeing temperature was varied from 20^{o}C to 100^{o}C using a series of dyeing to determine the effect of temperature on dye exhaustion. The results are represented in Figures 4.2 and 4.3 and summarized in Tables C1 and C2 respectively.

3.11.3 Effect of time on dyeing

Series of dyeing were carried out using 2% shade O.W.F at varying time from 20 minutes to 1 hour at an interval of 20 minutes each. The influence of dyeing time on dye exhaustion is represented graphically in Figures 4.4 and 4.5 and summarized in Tables C3 and C4 correspondingly.

3.11.4 Effect of pH on dyeing

The dyeing pH was varied at 4, 5, 6 and 7 pH in a series of dyeing to determine the effect of pH on dye exhaustion. The results are represented in Figures 4.6 and 4.7 and are summarized in Tables C5 and C6 respectively

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3.12 Fastness Properties

3.12.1 Wash fastness test

The I.S.O.3 standard procedure for washing was used to determine the wash fastness test. The washing conditions required or used are as follows:

Soda ash 2g/l

Soap 5g/l

Liquor ratio 50:1

Temperature $60 \pm 2^{o}C$

Time 30 minutes

A composite specimen was formed by stitching the dyed samples between two undyed pieces of polylactide and cotton fabric. The composite specimen was agitated in 100ml beaker containing the soap solution, plus other additives as mentioned above in the specified conditions of liquor ratio, temperature and time. The composite specimen was then removed, rinsed and the components separated and dried. The change in colour of the dyed samples and the staining of adjacent undyed cloths were assessed using the appropriate grey scale. The results are shown in Table 4.4

3.12.2 Fastness to perspiration (ISO-E04)

The test was carried out using the following solution:

(A) Alkaline solution

5 g/l sodium chloride

2.5g/l disodium hydrogen orthophosphate ($Na_2HPO_4.2H_2O$)

0.5g/l Histidine mono-hydrochloride monohydrate, ($C_6H_9O_2N_3.HCl.H_2O$).The solution was brought to pH 8 using 0.1N NaOH solution

(B) Acidic solution

5g/l sodium chloride, NaCl

2.2g/l sodium dihydrogen orthophosphate ($NaH_2PO_4.2H_2O$).

0.5g/l Histidine mono-hydrochloride – monohydrate, ($C_6H_9O_2N_3HCl.H_2O$). The solution was brought to pH 5.5 using 0.1N acetic acid solution.

The composite specimen was wetted out in the solution at a pH of 8 for alkaline in a liquor ratio of 50:1 and allowed it to remain for 30 minutes at room temperature. The specimen was placed between two plates of the perspirometer or a similar apparatus at a pressure of 12.5Kpa which was achieved by placing 4.5kg weight on the arranged samples in the perspirometer. The perspirometer set up was kept in the oven which temperature was set at 37^{o}C and was maintained for 4 hours. The procedure was repeated for the other composite specimens at a pH of 5.5 for acid and placed in another perspirometer. The samples were removed, opened up and allowed to dry at room temperature. Both specimens are then assessed for colour change of the test fabric and staining of the adjacent fabric. The results are shown in Table 4.5.

Plate 3.2: Perspirometer

3.12.3 Light fastness test (Nunn, 1979)

Using the standard ISO/ FDIS 105-B01, the dyed samples and blue wool standard were exposed facing due south and inclined at an angle to the horizontal approximately equal to the latitude of the place where the exposure is being made. Adequate ventilation of the samples during exposure was ensured. The partly covered samples were exposed to UV radiation. As exposure proceeded for 19 days, the samples under test and the blue wool standards were examined at intervals and the change in colour of the samples compared visually with the changes that occur in the standards. The light fastness of the sample is the number of the standard that shows a similar visual contrast between the exposed and unexposed part of the samples. The exposure was terminated when the blue wool standard 7 fades or when fully exposed and non-exposed test samples is equivalent to grade 3 on the grey scale. The results are shown in Table 4.6.

3.12.4 Sublimation fastness test

The composite of the dyed Polylactide fabric was placed in between a pair of hot plates equipped with electric heating system (Plate 3.3). The accurately controllable heating device was set at ISO temperature of 180 ±2^{o}C and a pressure of 40±2g/cm^{2}. The specimen was left for 30seconds under this condition and was removed and left for 4 hours at standard temperature of 20±2^{o}Cand relative humidity of 65±2%. The composite was then disassembled and changed in colour of sample and staining of undyed fabrics were assessed using grey scale for colour change and grey scale for staining respectively. The result is shown in Table 4.7.

Plate 3.3: Hot plate

3.12.5 Fastness to hot pressing (ISO 105-X11)

Three tests (dry, damp and wet pressing) were carried out here to investigate the hot pressing property of the dyed Polylactide fabric.

3.12.5.1 Dry pressing

The dyed specimen was placed on a piece of dry press cloth on a smooth horizontal surface. The hand iron at the selected temperature was placed on the specimen and left for 10 seconds. The specimen was then allowed to cool down at room temperature. Colour change and staining were examined using the appropriate grey scale.

3.12.5.2 Damp pressing

The dry specimen was placed on a dry press cloth and another dry piece of dry press cloth which was in distilled water at room temperature and extracted to 100% pick- up was placed over the test specimen. The hand iron at the selected temperature was placed on the specimen covered with the damp press cloth and was left for 10seconds. As usual the colour change and staining of adjacent undyed cloth were examined appropriately. The result is shown in Table 4.8

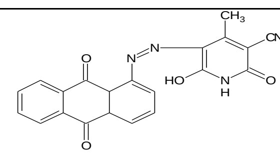
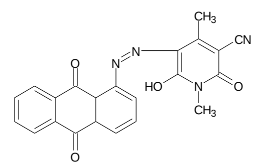
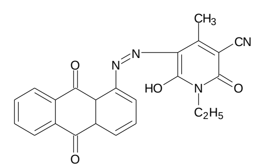
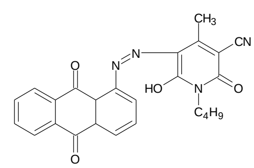
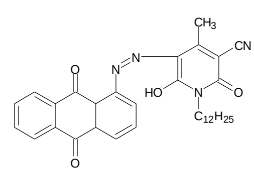
3.12.5.3 *Wet pressing*

The specimen and the piece of press cloth were saturated with distilled water at room temperature and were extracted to 100% pick – up. The specimen is then placed on a dry press cloth covered with wet press cloth. The hand iron at the selected temperature was placed on top for 15 seconds. Again change in colour and staining of adjacent cloth was examined appropriately.

CHAPTER FOUR

4.0 RESULTS

Table 4.1: Physical Characteristics of the synthesized dyes

Dye No	Molar Mass g/mol	Melting Point (^{O}C)	%Yield	Colour of The crystal	Colour of The Dyed Sample	Structure of The Dye
7a	386	320-322	77	Yellow	Yellow	
7b	400	310-311	72	Yellow	Lemon yellow	
7c	414	277-279	84	Yellow	Yellow	
7d	442	270-271	81	Yellow	Yellow	
7e	554	198-200	64	Yellow	Light yellow	

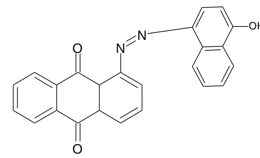
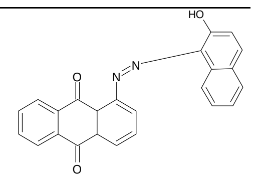
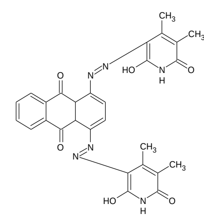
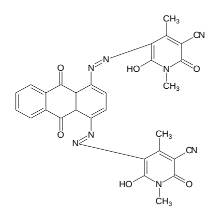
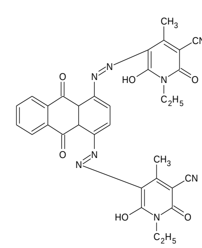
7f	380	217-219	68	Yellow	Light yellow	

Table 4.1 Continued

Dye no	Molar mass g/mol	Melting point (°C)	%Yield	Colour of the crystal	Colour of the dyed sample	Structure of the dye
7g	380	240-242	63	Red	Orange	
10a	540	133-135	72	Brown	Dark Brown	
10b	590	292-294	71	Red	Brown	
10c	618	244-245	74	Dark brown	Brown	

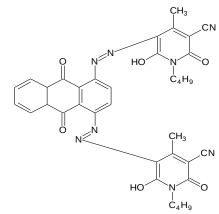
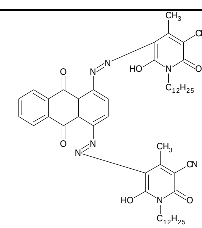
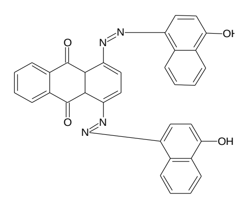
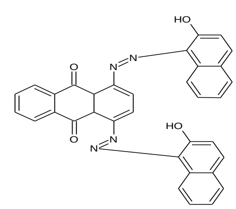
10d	674	232-234	67	Brown	Brown	

Table 4.1 Continued

Dye no	Molar mass g/mol	Melting point (^{o}C)	%Yield	Colour of the crystal	Colour of the dyed sample	Structure of the dye
10e	899	104-106	62	Light brown	Brown	
10f	550	165-168	63	Dark brown	Light brown	
10g	550	172-174	61	Brown	Light brown	

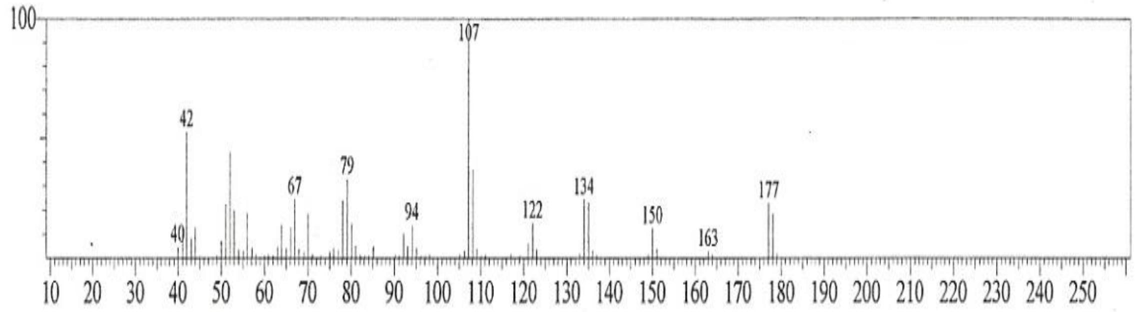


Figure 4.1: Mass spectra of 1-ethyl-2-hydroxyl-4-methyl-5-cyano-6-pyridone

Table 4.2 The Infra-Red spectral of the dyes

Functional group	Azo N=N	Carbonyl C=O	Nitrite C=N	Aromatic C-H	Aromatic C-C	m-Disubstituted	p-Disubstituted	O-H
Type of vibration	Stretching	Stretching	Stretching	Stretching	Stretching	Stretching	Stretching	Stretching
Dye no	-	-	-	-	-	-	-	-
7a	1515.99	1610.25 1705.64	2371.66 2337.59	3005	1460.23	680.12	816.49	3752.7 3620
7b	1515.4	1625.56 1704	2369.08	2980.82	1460.78	690.92	819.48	3951.04 3645.63
7c	1477.53	1659.16	2218.21 2486.33	2935.76	1477.52	705.97	853.53	3600.25 3775.75
7d	1520.21	1657.78	2372.63 2360.33	2925.73	1480.42 1465.84	680.1	814.4	3680.37 3651.61
7e	1520.68	1704.47	2370.97	2915.28	1478.93	-	817.36	3650.55
7f	1515.13	1656.82	-	2910.11	1455.83	680.28	816.21	3755.14
7g	1525.68	1659.97 1620.84	-	2905.33	-	-	836.98	3759.84 3681.79
10a	1520.45 1500.18	1705.68 1625.76	2370.91 2320.93	2900.15	1465.46	690.25	814.73	3753.1 3630.56
10b	1530.9 1505.18	1705,32 1670.98	2368.68 2325.46	2920.6 2900.18	1460.16	690.73	817.12	3752.16 3680.95
10c	1550.72 1500.05	1702.25 1650.74	2392.68 2398.67	2980.12 2920.18	1460.36	-	816.12	3759.8 3680.97
10d	1468.84	1650.46	3082.1	2940.58	1468.84	-	740.69	3421.83 3302.34
10e	1516.36 1480.85	1655.52 1690.98	2370.23 2339.18	2902.2	1480.85 1420.31	620.28 680.89	813.21	3752.17 3680.77
10f	1550.15 1516.29	1698.76 1656.39	-	2902.02	1480.1	-	814.53	3752.93 3682.25
10g	1525.65 1516.28	1705.46 1650.1	-	-	1460.78 1420.25	640.15	816.73	3751.79

Table 4.3: Spectroscopic properties of the dyes.

	Molar Extinction Coefficient in *DMF* x10^4 ($Lmol^{-1}cm^{-1}$)	λ max (nm) in DMF	λmax (nm) in Toluene	λ max (nm) in Ethanol (a)	λ max (nm) in ethanol + HCl (b)	Change in λ max (nm) (b-a)
7a	5.22	484	420	452	441	-13
7b	5.15	446	400	400	400	0
7c	3.95	483	401	420	404	-16
7d	2.97	486	459	463	463	0
7e	1.2	488	461	441	465	+24
7f	1.12	506	505	511	439	-72
7g	1.64	507	508	510	511	+1
10a	6.28	509	502	504	507	+3
10b	1.32	506	415	419	484	+65
10c	1.05	610	502	501	482	-19
10d	2.01	463	405	409	411	+2
10e	1.67	429	482	484	493	+9
10f	1.75	507	402	404	481	+77
10g	2.26	511	405	405	427	+22

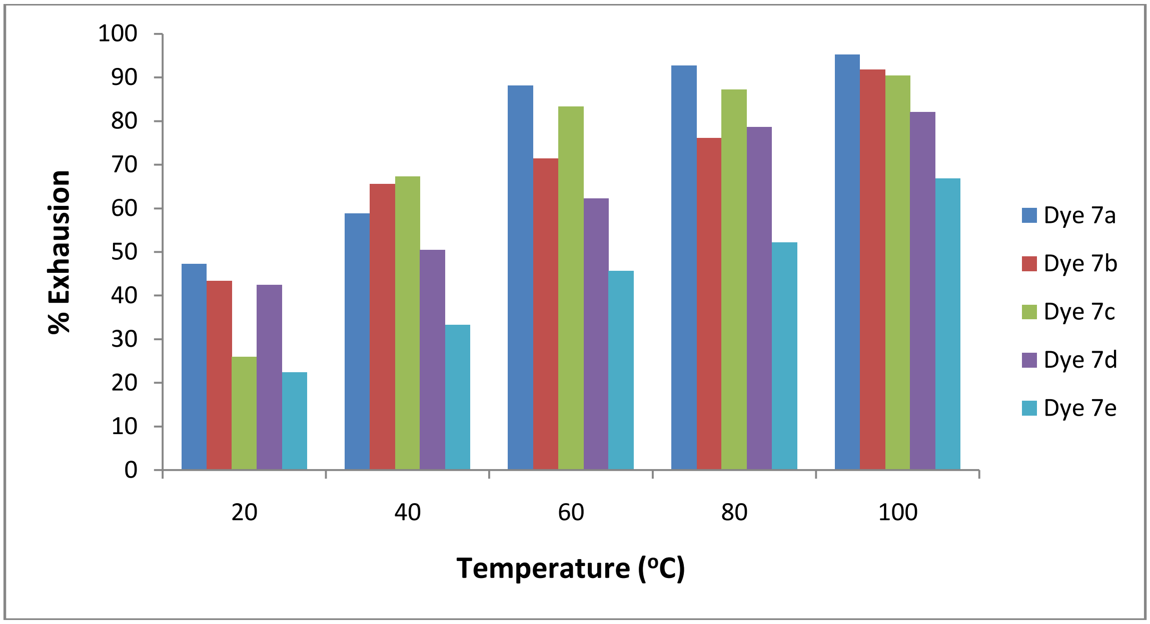


Figure 4.2: Effect of temperature on dye exhaustion for monoazo dyes (7a – 7e)

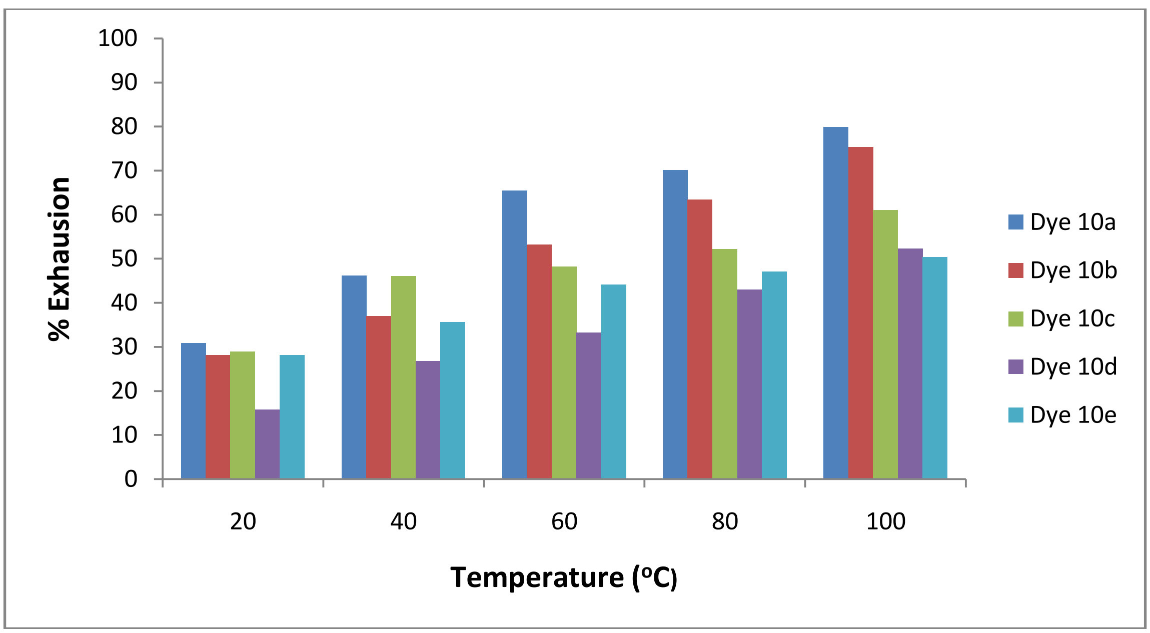


Figure 4.3: Effect of temperature on dye exhaustion for disazo dyes (10a – 10e)

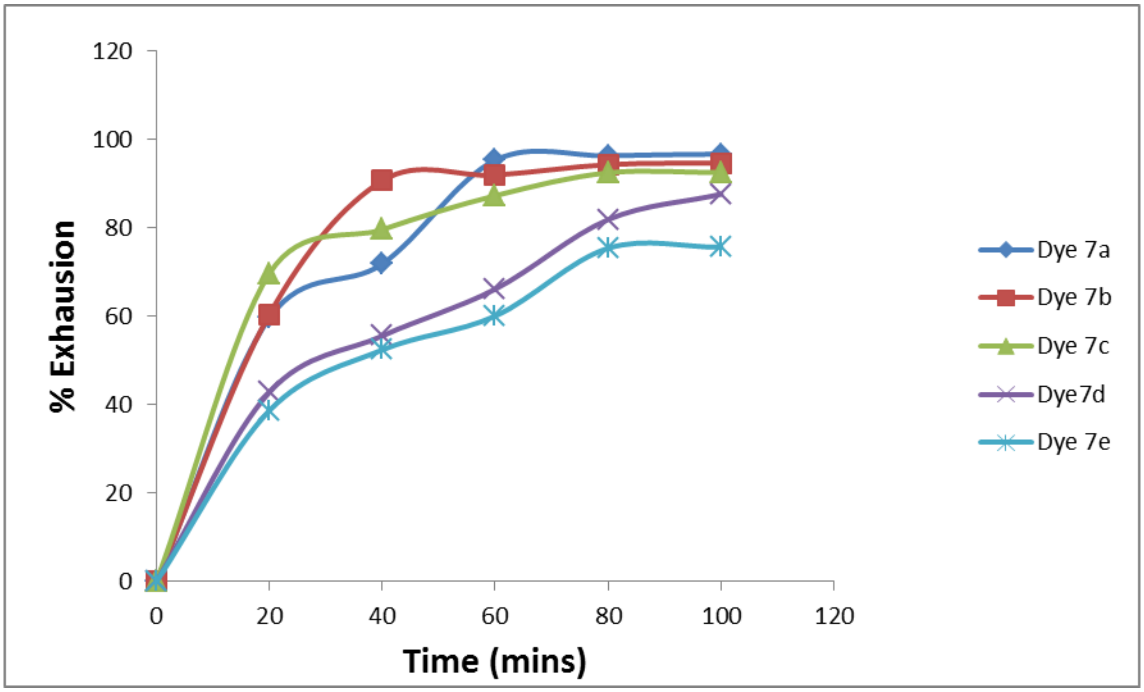


Figure 4.4: Effect of time on dye exhaustion for monoazo dyes 7a – 7e

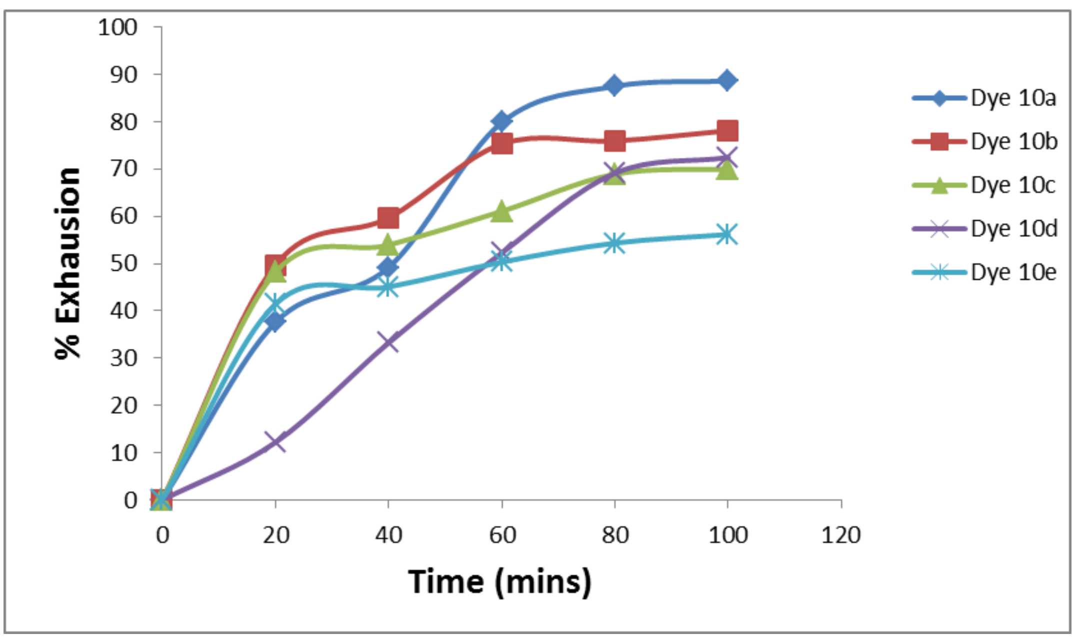


Figure 4.5: Effect of time on dye exhaustion for disazo dyes 10a – 10e

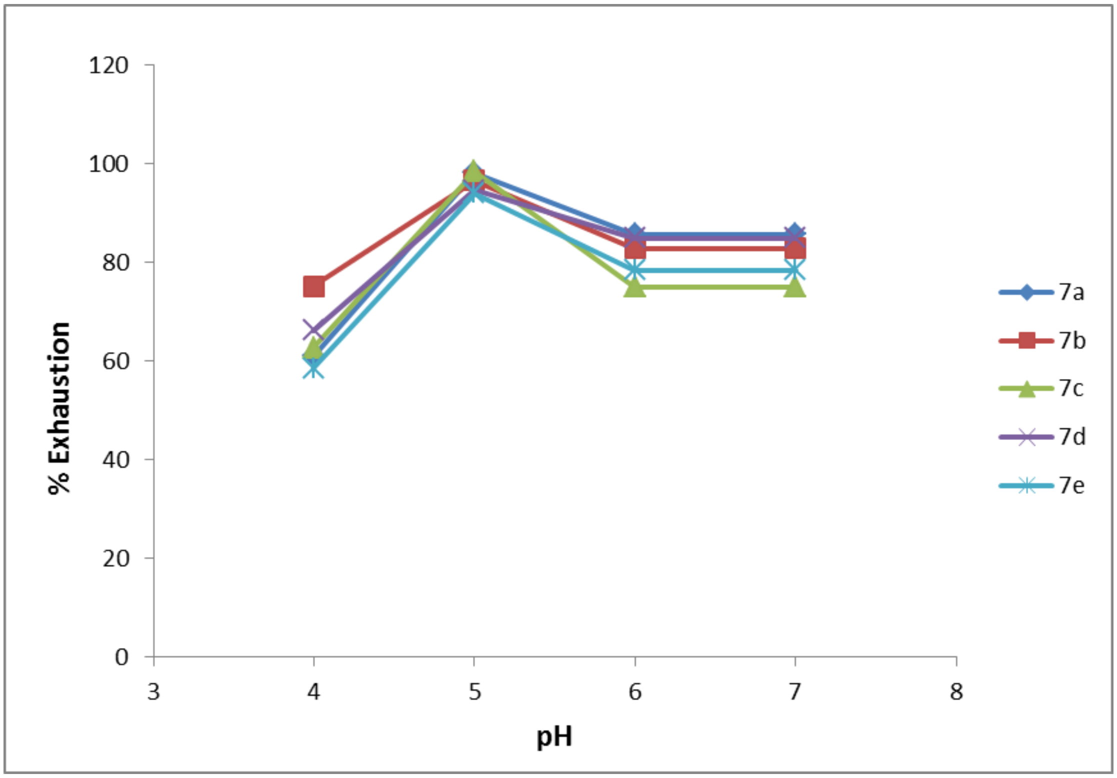


Figure 4.6: Effect of pH on dye exhaustion for monoazo dyes (7a – 7e)

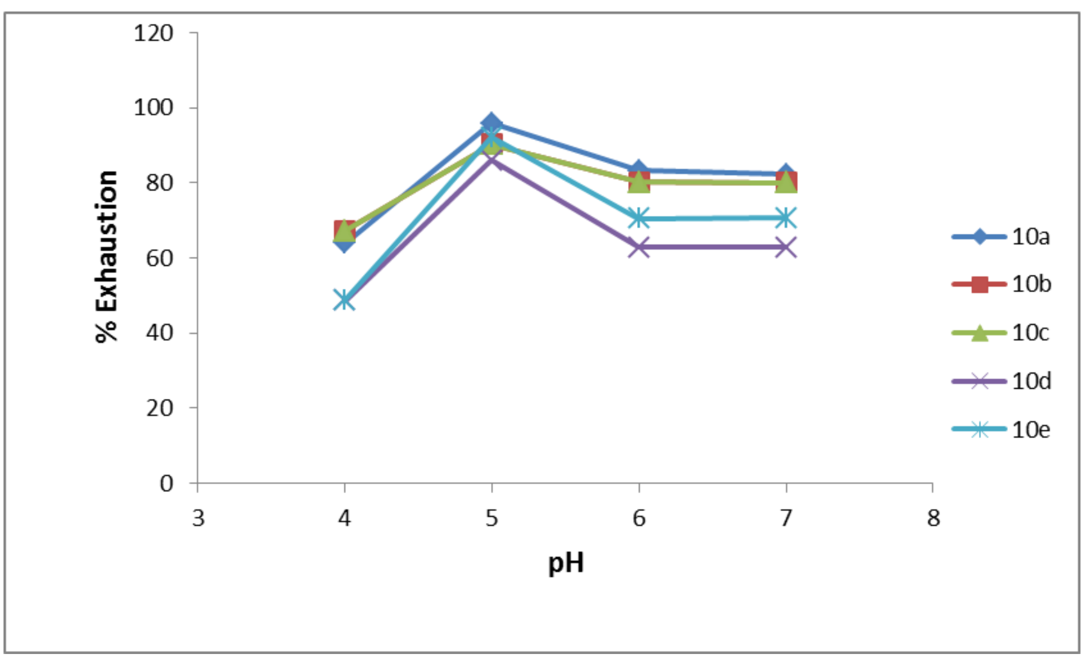


Figure 4.7: Effect of pH on dye exhaustion for disazo dyes (10a – 10e)

Table 4.4: Wash fastness ratings

Dye no	Change in shade	Staining on to cotton
7a	4	4
7b	4	4
7c	4	4
7d	4	4
7e	4	4
7f	4	4
7g	4	4
10a	3-4	3-4
10b	4	4
10c	4-5	4-5
10d	4	4
10e	4-5	4-5
10f	4-5	4-5
10g	4-5	4-5

Table 4.5:Perspiration Fastness ratings

	Alkaline		Acid	
Dye no	**Change in shade**	**Staining**	**Change in shade**	**Staining on to cotton**
7a	4	4	3-4	3-4
7b	4	4	4-5	4-5
7c	4	4	4	4
7d	4	4	4	4
7e	4	4	4	4
7f	4	4	4	4
7g	4	4	4	4
10a	3-4	3-4	3-4	3-4
10b	4-5	4-5	4	4
10c	4-5	4-5	4-5	4-5
10d	4-5	4-5	4	4
10e	4-5	4-5	4	4
10f	4-5	4-5	4	4
10g	4-5	4-5	4	4

Table 4.6: Light fastness ratings

Dye no	Change in shade
7a	6
7b	6
7c	6
7d	6
7e	6
7f	6
7g	6
10a	6
10b	6
10c	6
10d	6
10e	5
10f	6
10g	5

Table 4.7: Sublimation Fastness rating

Dye no	Change in shade	Staining on to cotton
7a	4	4
7b	3-4	3-4
7c	3-4	3-4
7d	4	4
7e	4	4
7f	4	4
7g	3-4	3-4
10a	3-4	3-4
10b	4-5	4-5
10c	4	4
10d	4-5	4-5
10e	4-5	4-5
10f	4-5	4-5
10g	4	4

	Dry pressing	Damp pressing	wet pressing

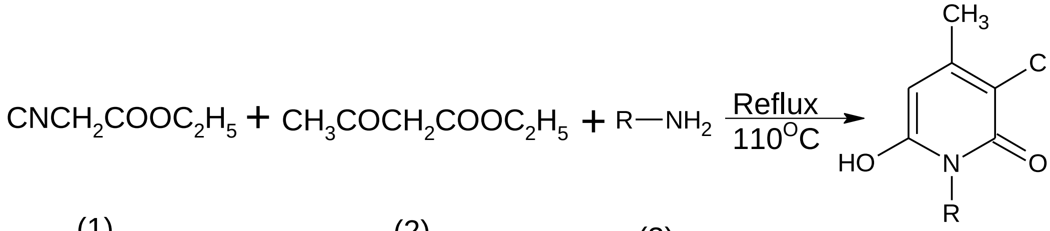
Table 4.8: Fastness to hot pressing ratings

Dye no	Change in shade	Staining	Change in shade	Staining	Change in shade	Staining
7a	4-5	4-5	4-5	4-5	4-5	4-5
7b	4-5	4-5	4-5	4-5	4-5	4-5
7c	4-5	4-5	4-5	4-5	4-5	4-5
7d	4-5	4-5	4-5	4-5	4-5	4-5
7e	4-5	4-5	4-5	4-5	4-5	4-5
7f	4-5	4-5	4-5	4-5	4-5	4-5
7g	4-5	4-5	4-5	4-5	4-5	4-5
10a	4-5	4-5	4-5	4-5	4-5	4-5
10b	4-5	4-5	4-5	4-5	4-5	4-5
10c	4-5	4-5	4-5	4-5	4-5	4-5
10d	4-5	4-5	4-5	4-5	4-5	4-5
10e	4-5	4-5	4-5	4-5	4-5	4-5
10f	4-5	4-5	4-5	4-5	4-5	4-5
10g	4-5	4-5	4-5	4-5	4-5	4-5

CHAPTER FIVE

5.0 DISCUSSION

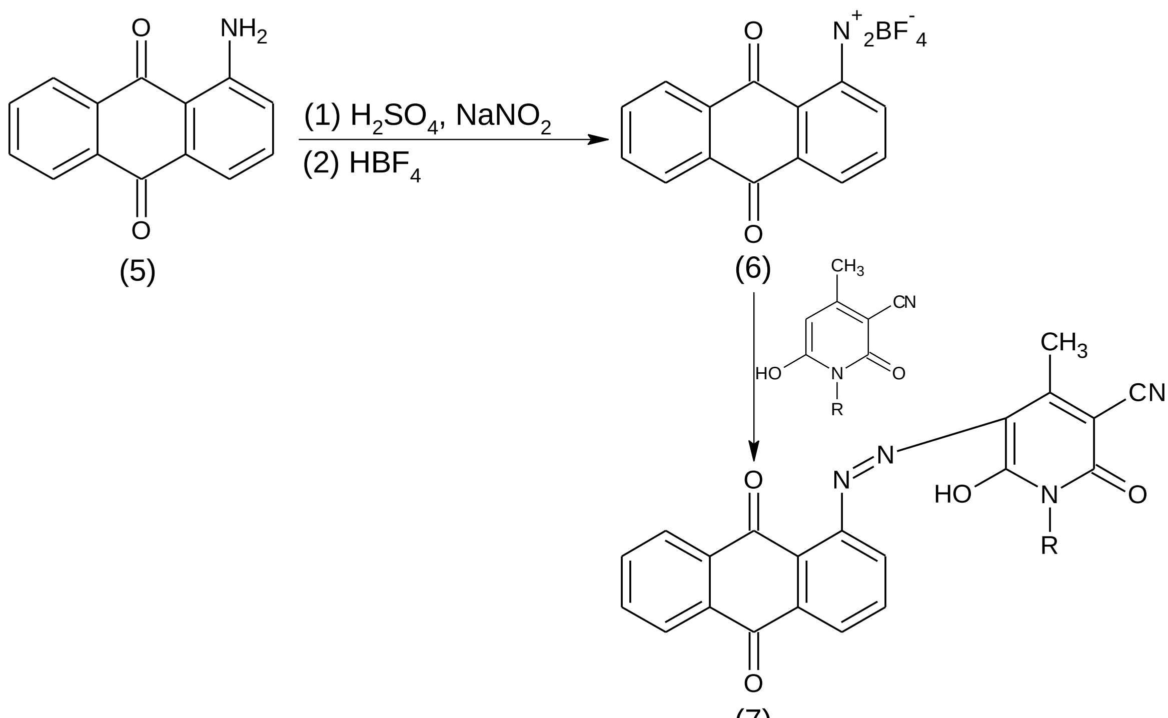
5.1 Summary of the Synthetic Routes of Dye Intermediate and Dyes



(1) (2) (3) (4)

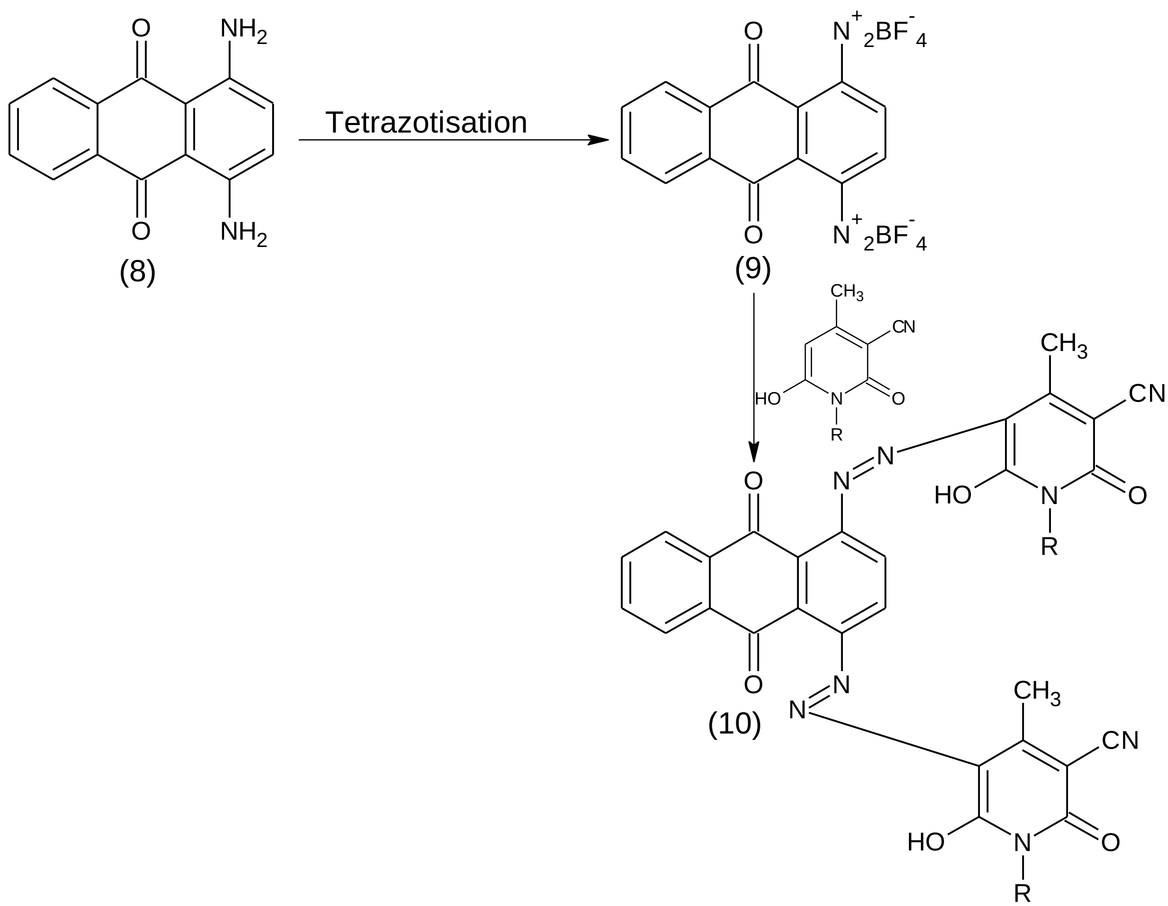
R (a) = H
(b) = CH_3
(c) = C_2H_5
(d) = C_4H_9
(e) = $C_{12}H_{25}$

Scheme 5.1: Synthetic route for dye intermediates



(5) (6) (7)

Scheme 5.2: Synthetic route for mono azo dyes



Scheme 5.3: Synthetic route for disazo dyes

5.2 Synthesis of Coupling Components

The synthetic route for the synthesis of the coupling components is shown in Scheme 5.1 Five coupling components were synthesized in this study. Each of which was synthesized by heating a mixture of ethylcyanoacetate, ethylacetoacetate and the corresponding alkylamine at 110°C for nine hours under reflux. The first coupling component to be synthesized was 1-amino-2-hydroxy-4-methyl-5-cyano-6-pyridone (4a) which was obtained by heating a mixture of ethylcyanoacetate, ethylacetoacetate and ammonium hydroxide. This reaction produced a white crystalline solid which has a molar mass of 150, 65% yield and it's melting point was 305°C. By replacing ammonium hydroxide in the first synthesis with methylamine the second coupling component obtained was 1-methyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4b). It was a white crystalline solid having a molar mass of 164, 72% yield and melting point of 295°C. Using ethylamine as the third component of the heated mixture, 1-ethyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4c) was synthesized. It was a white crystalline solid with a molar mass of 178, 85% yield and melting point of 245°C. In the same vein, 1-butyl-2-hydroxy-4-methyl-5-cyano-6-pyridone (4d) was synthesized using butylamine in the reacting mixture. The results gave also a white crystal, molar mass of 206, 74% yield and a melting point of 138°C. The last coupling component is 1- dodecyl-2-hydroxy-4-methyl-5-cyno-6-pyridone (4e) which was synthesized using dodecylamine as the third reacting mixture. A white crystal was also obtained, molar mass of 318, it's yield was 74% and it's melting point was 98°C.

5.3 Syntheses of the Dyes

The dyes synthesized were obtained by diazotising 1-aminoanthraquinone and tetrazotising 1,4-diaminoanthraquinone as shown in scheme 5.2 & 5.3 respectively, which were the two primary aromatic amines used. The diazonium ion was salted out using tetrafluoroboric acid. The diazonium salts was each coupled to the five coupling components obtained above to get five monoazo dyes (7a-7e). Likewise the tetrazonium salt obtained from 1,4-diaminoanthraquinone was coupled to each of the above synthesized coupling components to get five disazo dyes. However, the diazonium salt was coupled to 1-naphthol and 2-naphthol to obtain dyes 7f and 7g. Also, the tetrazonium salt was coupled to 1-naphthol and 2-naphthol to obtain dyes 10f and 10g. A total of fourteen dyes were synthesized altogether as shown in Table 4.1. The yields of the dyes were satisfactory (ranging from 64 – 84%), the melting point were examined and reported in Table 4.1. The colours of crystals obtained were ranges of yellow for the monoazo dyes and light to deep brown for disazo dyes. Also obtained was orange colour from diazonium salt coupled with 2-naphthol.

5.4 Assessment of Mass Spectra

A mass spectrum is a plot of relative ion abundance versus mass-to-charge ratio (m/z) (William *et al*, 2012). It is the presentation of the masses of the positively charged fragments including the parent ion versus their relative concentration, when an electron beam in a mass spectrometer bombards a substance under investigation, the spectrometer, quantitatively records the m/z results as a spectrum of positive ion fragments. The peak from most abundant cation is called the base peak and is assigned an arbitrary intensity of 100. The relative abundances of all other cations in a mass spectrum are reported as percentages of the base peak including the parent peak.

The identified mass spectral of 1-ethyl-2-hydroxyl-4-methyl-5-cyano-6-pyridone with mass-to-mass ratio (m/z) of 40, 42, 43, 66, 78, 93, 107,150 and the parent 178 representing M and the corresponding positive charge fragments of C_3H_4, CNO^+, $CHNO^+$, C_3NO^+, $C_5H_4N^+$, $C_5H_3NO^+$, $C_6H_5NO^+$,M^+-C_2H_4 are shown respectively in Figure 4.1.

The molecular weight determination by mass spectroscopy may not be the same as that calculated from atomic weights, if parent compound contains certain elements with high isotopic abundances (Khopkars, 2008).This may account for the slight difference/change in numerical value of molecular weights of the samples under examination. Also the difference in melting points of the tested samples and the column oven temperature may also account for the inaccuracy/variation of structures, as the melting points of samples should be considered before injecting the samples.

5.5 FT-IR Analysis of the Synthesised Dyes

The absorption of infra-red radiation resulting from atom containing in the molecules showed the functional group present in the molecule of the compound synthesized (silverstein *et al*., 1977). There are two regions of the infra-red spectrum of interest to the organic chemist; these are the functional group and the finger print regions. The functional groups region extends from 4000-450cm^{-1} and the finger-print region extends from 1450-600cm^{-1}. In this functional group region are found absorption bands due to the stretching frequencies of various functional groups such as CH, OH, NH and so forth. This is the most vital region of the spectroscopic analyst, because from the position of the peaks inferences can be made of the functional groups that are present and those which are absent. While the finger-print region contains certain functional group absorptions may be spotted in this region. It is most useful for comparison purpose. In fact, all organic compounds have a unique infra- red spectrum.

Each of the dyes synthesized gave characteristic absorption peaks in the finger print region and also in the functional groups regions. As can be seen from the infra-red spectrum results in Table 4.2, all the dyes gave absorption peaks due to azo group, -N=N- stretching vibration at 1450-1510cm^{-1}; aromatic C-H stretching vibration bands appeared in the region of 3030-2900cm^{-1}; C≡N stretching vibration bands appeared in the region of 2260-2220cm^{-1}, C-C stretching vibration bands appeared in the region of 1450 -1600cm^{-1}; C=O stretching vibration bands appeared in the region of 1680-1780cm^{-1}; O-H stretching vibration bands appeared in the region of 3890-3650cm^{-1}; respectively. However, m-disubstituted of the pyridones exhibited a vibration stretching band of 680 - 725 cm^{-1}, while the p-disubstituted of the disazo dyes is responsible for the vibration band of 800-860cm^{-1} (Graham and Craig, 2012). The FTIR spectral of the dye intermediate are shown in Appendix A while the FTIR spectra of the dyes are shown in Appendix B.

5.6 Visible Absorption of the Synthesized Dyes

The visible absorption spectral of the dyes were measured in ethanol, toluene, dimethylformamide (DMF). The wavelength of maximum absorptions were highest in DMF, because DMF is the most polar of these solvents. The molar extinction coefficient (ε) was calculated using DMF as solvent. The results of UV- spectra are summarized in Table 4.3.

Ultraviolet – visible absorption are indicative of electron transition between the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). All the compounds showed absorption in the visible region greater or equal to 400nm which were characteristic of all compounds of the dyes studied. From the results in Table 4.3, the mono azo dyes 7a, 7b, 7c,7d and 7e absorbed maximally at 484nm, 446nm, 483nm, 486nm and 488nm respectively in DMF. Dye 7e is bathochromic compared with dyes 7a, 7b, 7c and 7d as it absorbed at longer wavelength. Dye 7e was made from the coupling component of 1-dodecyl-2- hydroxyl -4-methyl-5-cyano-6-pyridone which contains longer alkyl group in its molecule. This is followed by dye 7d containing 1-butyl-2-hydroxyl-4-methyl-5-cyano-6-pyridone as coupling component which absorbed at 483nm and is bathochromic compared with dyes 7a, 7b and 7c which absorbed at 484nm, 446nm, 483nm respectively. Dye 7b absorbed at 446nm is more hypsochromic than dye 7a which absorbed at 484nm as it absorbed at lower wavelength. Also dye 7g which absorbed at 507nm is more bathochromic than dye 7f which absorbed at 506nm, the two dyes were made from the coupling components of β –naphthol and α–naphthol respectively. However, the monoazo dyes (7a- 7e) absorbed highest λmax in DMF (484nm, 446nm, 483nm, 486nm 488nm, respectively) than that of toluene (420nm, 400nm 401nm, 459nm, 461nm respectively) and in ethanol (452nm, 400nm, 420nm, 463nm, 441nm, respectively) except dyes 7f and 7g which absorbed highest in ethanol (511nm and 510nm respectively), absorbed at 505nm and 508nm in toluene, 506nm and 507nm in DMF respectively.

As presented in Table 4.3, the disazo dye 10c absorbed at 610nm in DMF , hence bathochromic compared to other disazo dyes 10a, 10b, 10d, 10e, 10f and 10g that absorbed at 509nm, 506nm, 463nm, 429nm, 507nm and 511nm respectively. Meanwhile dye 10a was more bathochromic than dye 10b by +3 in DMF (509nm and 506nm respectively) and dye 10d which absorbed at 463nm was more bathochromic than 10e which absorbed at 429nm by +14, both in DMF. Dye 10f absorbed at 507nm and was hypsochromic than dye 10g which absorbed at 511nm by -14 in DMF. Generally, the disazo dye having the same coupling component as in monoazo dye absorbed bathochromically at higher wavelength than the corresponding monoazo dyes in the three solvents, for example, 10a absorbed at 509nm and 7a absorbed at 484nm, dye 10b absorbed at 506nm and 7b absorbed at 446nm, dye 10c absorbed at 610nm and dye 7c absorbed at 483nm and so forth, except dyes 10d which absorbed at 463nm and 10e absorbed at 429nm both absorbed hypsochromically relative to their corresponding monoazo dyes 7d that absorbed at 486nm and 7e which equally absorbed at 461nm in DMF. Spectrophotometric measurements therefore showed that the spectra of the disazo dyes possesses visible absorption peaks whose intensity changes with the polarity of the solvent. This is probably due to the aggregation of the dyes. While the bathochromic shift of the disazo in relation to the monoazo and vice versa may be attributed to the increase in conjugation between the two parts of the dyes.

5.6.1 Solvatochromic effects

Solvatochromism is the ability of a chemical substance to change colour due to change in solvent polarity. With increasing polarity of the solvent, the absorption maximum is shifted to longer wavelengths (Marini and Munoz, 2010). Usually, in many dye molecules the ground state is less polar than the excited state so that the polar solvent will tend to stabilize the excited state more than the ground state leading to bathochromic shift in the visible absorption maximum, which is termed positive solvatochromism. The interaction of the solvent with the dye molecule is greater in polar solvent (Reichardt and Welton, 1991).

The phenomenon of solvatochromism arises from a change in the electronic structure and distribution of charge of the excited state as compared with the ground state. If the excited state is more polar than the ground state, it will be better stabilized by polar solvation and its energy lowered, so that the transition will occur at longer wavelengths, i.e. there will be a bathochromic shift (red shift) with increasing solvent polarity (Marini and Munoz, 2010). Most of the shifts in maximum absorption wavelength observed were bathochromic for majority of the dyes where measurements were done in solvent of higher polarity. The maximum absorption wavelengths values shifted to longer wavelengths when the solvent was changed from ethanol to dimethylformamide (DMF), for example, dye 7a absorbs at 420nm in toluene, 452nm in ethanol and 484nm in DMF. Likewise, dye 10d absorbs at 405nm in toluene, 409nm in ethanol and 463nm in DMF. Also dye 7c absorbs at 401nm, 420nm, 483nm in toluene, ethanol and DMF respectively. Dyes 10e, 10f and 10g absorb respectively at 482nm, 402nm and 405nm in toluene, 484nm, 404nm and 405nm in ethanol and 429nm, 507nm and 511nm in DMF. Although some of the dyes had negative solvatochromism, that is a hypsochromic shift to lower wavelength in the visible absorption spectrum when the solvent was changed from ethanol to DMF for example, dyes 7f, 7g and10e changed from 511nm to 506nm, 510nm to 507nm, 510nm to 505nm and 510nm to 505nm respectively. Dyes 7c and 10c showed a negative solvatochromism when the solvent was changed from toluene to ethanol as indicated, 7c changed from 420nm to 401nm and 10c changed from 502nm to 501nm. However dye 7b showed no solvation when the solvent was changed from toluene to ethanol, it absorbs at 400nm in both toluene and ethanol.

Solvent polarity effects on visible absorption band of dyes have been thoroughly studied and well documented in literature (Venkatarama, 1972). The literature reported that π-----→π* transition exhibits bathochromic effect when the polarity of the solvent is increased while n----→π* transition shows hypsochromic effect with increase in solvent polarity. This is a clear indication that in this study, the visible band is due to π----→π* transition since a positive solvatochromism occurred in some of the dyes and n----→π* transition since a negative solvatochromism also occurred in some of the dyes. Solvatochromism is due to various solute-solvent interactions in both the ground and excited states. The red shift observed on changing to a polar solvent suggests that the dye molecules has a more polar excited state than the ground state and this will lower the energy of the π----→π* transition. Thus the energy difference between the ground and the excited state is reduced leading to a bathochromic shift of the visible band.

5.6.2 Effect of acid on visible absorption band (Halochromism)

The effect of few drops of acid (HCl) on the visible absorption band, which could decrease or increase the maximum absorption wavelengths, is referred to as halochromism. The increase of λmax in acidic medium is referred to as positive halochromism while the decrease in λmax in same acidic medium is referred to as negative halochromism. The effect of few drops of acid on ethanol solution of the dyes was inspected and the results are summarized in table 4.3. Among the synthesized dyes, dyes 7e, 7g, 10a, 10b, 10d, 10e, 10f and 10g exhibit positive halochromism as they absorbed at 441nm, 510nm, 504nm, 419nm, 409nm, 484nm, 404nm and 405nm respectively in neutral solution of ethanol and absorbed maximally at 465nm, 511nm, 507nm, 484nm, 411nm, 493nm, 481nm and 427nm respectively in acidic solution of ethanol, indicating a bathochromic shift of +24, +1, +3, +2, +9, +77 and +22nm in that order. However, some of the dyes showed a negative halochromism. For example,, dyes7a, 7c and 10c absorbed in neutral ethanol solution at 452nm, 420nm and 501nm but absorbed maximally at 441nm, 404nm and 482nm in acidic solution of ethanol, indicating a hypsochromic shift of -13, -16 and -19nm respectively. Dyes 7b and 7d showed no halochromism effect as they both absorbed at 400nm and 463nm respectively in both neutral and acidic solution of ethanol.

5.6.3 The molar extinction coefficient (ε)

The molar extinction coefficient (ε) is a constant for each molecule of any given wavelength representing the absorbance in 1cm thickness of a medium containing 1 mole of the absorbing substance per litre (Giles, 1974).The molar extinction coefficient is actually a measure of the probability that photon of the correct wavelength striking the molecule will be absorbed (Mclaren, 1983).

Extinction coefficient (ε) was calculated using the relationship:

$\mathrm{Log}_{10}\, I_0 / (I = \varepsilon cl)$……………….. (3.1)

Where:

[Io/I] = Absorbance A or optical density

Io = Intensity of incident light

I = Intensity of transmitted light

ε = Extinction Coefficient

$A = \varepsilon c l$ ……………………….. (3.2)

$\varepsilon = A/(c l)$ ……………………….. (3.3)

Where:

ε	=	Extinction Coefficient
A	=	Absorbance at λ max
c	=	Concentration of dye in mol/dm3 and
l	=	Path length.

The molar extinction coefficient was calculated based on the concentrations of the dyes in DMF as a solvent. The molar extinction coefficient, also a measure of the amount of light absorbed by a compound in solution, was calculated for each dye. From the results in Table 4.3, it could be seen that dyes (7a, 7b, 7c, 7d and 7e) possessing high molar extinction coefficient appear on the fabric brighter. This may be attributed to the fact that they transmit more light in comparison to others and therefore have narrow absorption bands with sharp peaks as compared to others.

5.7 Effect of Temperature on Dye Exhaustion.

Temperature affects the rate of dye exhaustion since diffusion is directly proportional to the thermodynamic temperature. The higher the temperature of the dye bath the greater the kinetic energy of the dye molecules and the faster the diffusion of the dye molecules in and out of the substrate. Increase in temperature also tends to increase fabric porosity by increasing the molecular entropy and amorphous region of fabric polymer matrix. From Tables C1 and C2 in Appendix C, temperature was varied at constant time of dyeing and liquor ratio, it was observed that increase in temperature increases the dye exhaustion. A rise in temperature increases exhaustion rather than diminishes (Giles, 1974), therefore, the exhaustion was greater at higher temperature. It was observed that the mono azo dyes had higher exhaustion values than their corresponding disazo dyes this may be attributed to increase in mobile amorphous phase of the fibre and dyes molecular sizes. It has been investigated in the recent study (Mohammed *et al*., 2011) that in the cause of investigating PLA crystallization that mobile amorphous phase increased as the dyeing temperature increased. The monoazo dyes have a smaller molecular size relative to their corresponding disazo dyes hence may had diffused faster and much of its molecules may have been retained in the fabric. The effect of temperature on dye exhaustion for monoazo dyes (7a, 7b, 7c, 7d, and 7e) and disazo (10a, 10b, 10c, 10d and 10e) are shown in Figures 4.2 and 4.3 respectively. Clearly it can be seen in Tables C1 and C2 by comparism that dye 7a exhausted better than dye 10a with percentage exhaustion values of 95.25% and 88.62% respectively, dye 7b exhausted better than 10b and dye 7c was better exhausted than dye 10c and so forth.

5.8 Effect of Time on Dye Exhaustion

From Tables C3 and C4 time was varied, the temperature was kept constant at $100^{o}C$ and the liquor ratio was 50:1. It was observed that increase in time of dyeing increases the exhaustion. The reason may be at shorter time of dyeing the dye exhaustion was fairly achieved but at higher time of dyeing the exhaustion may be fully achieved. At the initial stage of the dyeing only few of the dye molecules may have dissolved inside the water as disperse dyes are known to have low solubility in water and dyeing takes place from a monomolecular dilute solution of the dye in water, the concentration of which was maintained by the progressive dissolution of solid dye from the finely dispersed dye particles in suspension. With time, the molecules of dye are transferred from solution to the surface of the fabric and adsorbed dye diffused monomolecularly into the fabric to form a solid solution (Nkeonye, 1987). From Tables C3 and C4 graphically represented in Figures 4.4 and 4.5, it can be seen for all the dyes that as the dyeing time increases, the percentage exhaustion as well as the depth of shade on the fabric increase. The monoazo dyes attained equilibrium at faster time of 60 minutes compared to the disazo dyes which attained equilibrium at 80 minutes. This may be attributed to size of the dye molecules. The disazo dyes are bigger molecularly than there corresponding monoazo dye, they may have diffused slower and must have taken more time to reach equilibrium. Among the monoazo dyes (7a, 7b, 7c, 7d and 7e), dye 7a diffused faster and exhausted better. This was followed by dye 7b and dye7c respectively. Dye 7e which contains the longest alkyl chain in the pyridone diffused slowest and exhausted less than other monoazo dyes. The disazo dyes (10a, 10b, 10c, 10d and 10e) also follow this same trend with dye 10a diffused faster and exhausted better. While dye 10e having the longest alkyl chain group in it molecule diffused slowest and exhausted less than the other disazo dyes. All these observation may be attributed to the molecular size of dyes' molecules.

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5.9 Effect of pH on Dye Exhaustion

Figures 4.6 and 4.7 show the effect of pH on dyeing exhaustion of the azo dyes and the disazo dyes respectively at 100^{o}C for 60 minutes. It was observed that there was an increase in dyeing exhaustion at pH 4-5 and then subsequent decrease in exhaustion above the pH of 5. This may be attributed to achieving the dye solubility at pH of 5 which is a commonly used level for the application of disperse dyes in batch dyeing procedures (Liang, 2010). Also the decrease in dyeing exhaustion observed at pH greater than 5 may be as a result of loss of fibre strength and elongation. Tables C5 and C6 show the results of changed in dye exhaustion as a result of changed in pH.

5.10 Assessment of Washing Fastness

The resistance of dyeing materials to laundry treatment such as washing is referred to as washing fastness. This is very important and there are several washing tests that are applied according to the purpose for which the material is intended. Using ISO wash test NO.3, it can be observed in Table 4.4 that the washing fastness is generally good with little or no stain on adjacent fabric. The ratings vary from good to very good for the monoazo dyes (7a – 7g) and disazo dyes (10b – 10g). Only dye10a shows the moderate rating of 3 – 4 while others show rating greater than 4 which is a very good result. Generally, the good washing fastness observed with the synthesized dyes may be attributed to the difficulty generally encountered by disperse dyes in their diffusion into Polylactide fibre, meaning that once in, migration of the dye out of the fibre, will equally be difficult, thereby giving dyeing of high fastness to washing. It was also observed that disazo dyes 10c, 10d, 10d, 10e, 10f and 10g show better fastness to washing than the monoazo dyes 7a, 7b, 7c, 7d, 7e, 7f, and 7g. This may be attributed to the bigger molecular sizes of the disazo dyes than the monoazo dyes which may have found it difficult to diffuse into the fibre and hence find it difficult to migrate out of the fibre.

5.11 Assessment of Fastness to Perspiration

The result of fastness to perspiration is almost similar to washing fastness. The results shown in Table 4.5 indicated good perspiration fastness properties in both acidic and alkaline solutions. Again only dye 10a showed a lower moderate rating of 3 - 4 while others have greater than 4 rating.

5.12 Assessment of Fastness to Light

Light fastness is the resistance of colour of dyeing materials to the influence of light. The fastness test can be done using day light for a long period or by a xenon arc, which is the accelerated version of the test (Marsh, 1966).

In the present studies day light was employed, the dyed samples were exposed to daylight alongside with eight blue wool standards and the results are shown in Table 4.6. The fastness to light of dyed fibre depends on many factors, the most important of which are the inherent photo stability of the dye chromophore and the way in which this stability is affected by the chemical nature of the substrate. The results of light fastness summarized in Table 4.6 indicated good to very good fastness to light. The rating of 6 meaning very good was obtained on all the monoazo and almost all the disazo dyes except dyes 10e and 10g which were both given a rating of 5 meaning good in the standard ratings. However, other higher ratings include 7 which is excellence, 8 is the maximum light fastness. Rating of 1 is very poor, while ratings 2, 3 and 4 are poor, moderate and fairly good respectively. Generally, all the synthesised dyes show very good fastness properties to light fastness. The result may be attributed to the molecular structure of the dyes, planarity and dye substituents that provided shield from radiant energy on azo chromophores. Therefore, this effect conferred good light fastness properties on the dyes.

5.13 Assessment of Fastness to Sublimation

Sublimation, or dry heat, fastness can be an important property of disperse-dyed Polylactide because of the use of heat treatments in the finishing of the fabric; disperse dyes must be small, non-ionic molecules of low molecular weight. As such, they often exhibit a significant vapour pressure. Therefore, if heat treatments during fixation, or subsequently, for example, ironing, are involved, the dye may sublime and cause contamination of equipment or adjacent undyed material (Gordon & Gregory). The heat fastness of dyeings of equal dye concentration on the same substrate will, at a specific temperature and time, be dependent on the size and polarity of the molecules of the dyes involved which in turn determine the rate of diffusion of the dye within the substrate and the volatility of the dye. Increases in size and/or polarity will tend to reduce the rate of diffusion out of the fibre and the vapour pressure of the dye and thus increase sublimation. The fastness of the dyed fabrics to sublimation was generally very good for both the monoazo and disazo dyes as shown in Table 4.7.

5.14 Assessment of Fastness to Hot Pressing

Fastness to hot pressing follows a similar trend with fastness to sublimation. Table 4.8 shows the result of fastness to hot pressing to be very good. The result indicated that both monoazo and the disazo dyes have ratings of 4-5 which is a very good result. An indication of excellent fastness property of all the synthesised dyes to hot pressing.

CHAPTER SIX

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

New disperse dyes with high affinity for Polylactide fabric has been synthesized from low cost pyridone as a coupling component. Previous studies indicate that pyridones have been synthesized in the presence of ethanol and piperidine as a catalyst which is very expensive and difficult to obtain. In this study the pyridone derivatives were synthesized from the mixtures of ethylacetoacetate, ethylcyanoacetate and the corresponding alkyl amine only. The results showed high exhaustion on PLA and the dyed fabric has good fastness properties.

6.2 Recommendations

A lot of researches are going on PLA, the interest and the development are growing by the day because of it availability and low cost of production for instance, NatureWork LLC of USA has over the past few years developed large-scale operation for the production of PLA polymer used for packaging and fibre application. However these products have to be coloured or dyed. To meet up with these rapid demand research has to be intensified on the synthesis of substantive disperse dyes for the fibre and as pigments for other materials to enhance their appearances. Furthermore, the tinctoral strength of these synthesized dyes are very high although they are mostly yellow, especially the monoazo dyes (7a – 7e), but their stain ability with any material in contact is very high, they were hardly or not removable hence the viability of these dyes to be used as a pigments for plastic, rubber and even paint should be investigated in another study since their fastness properties have been investigated and are found to be very good. Also these dyes are recommended to be applied on other synthetic fibres such as polyester and nylon may be there can be improvements on the existing synthesized disperse dyes for these mentioned fibres.

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APPENDICES

Appendix A: FT-IR Spectral for Dye Intermediates

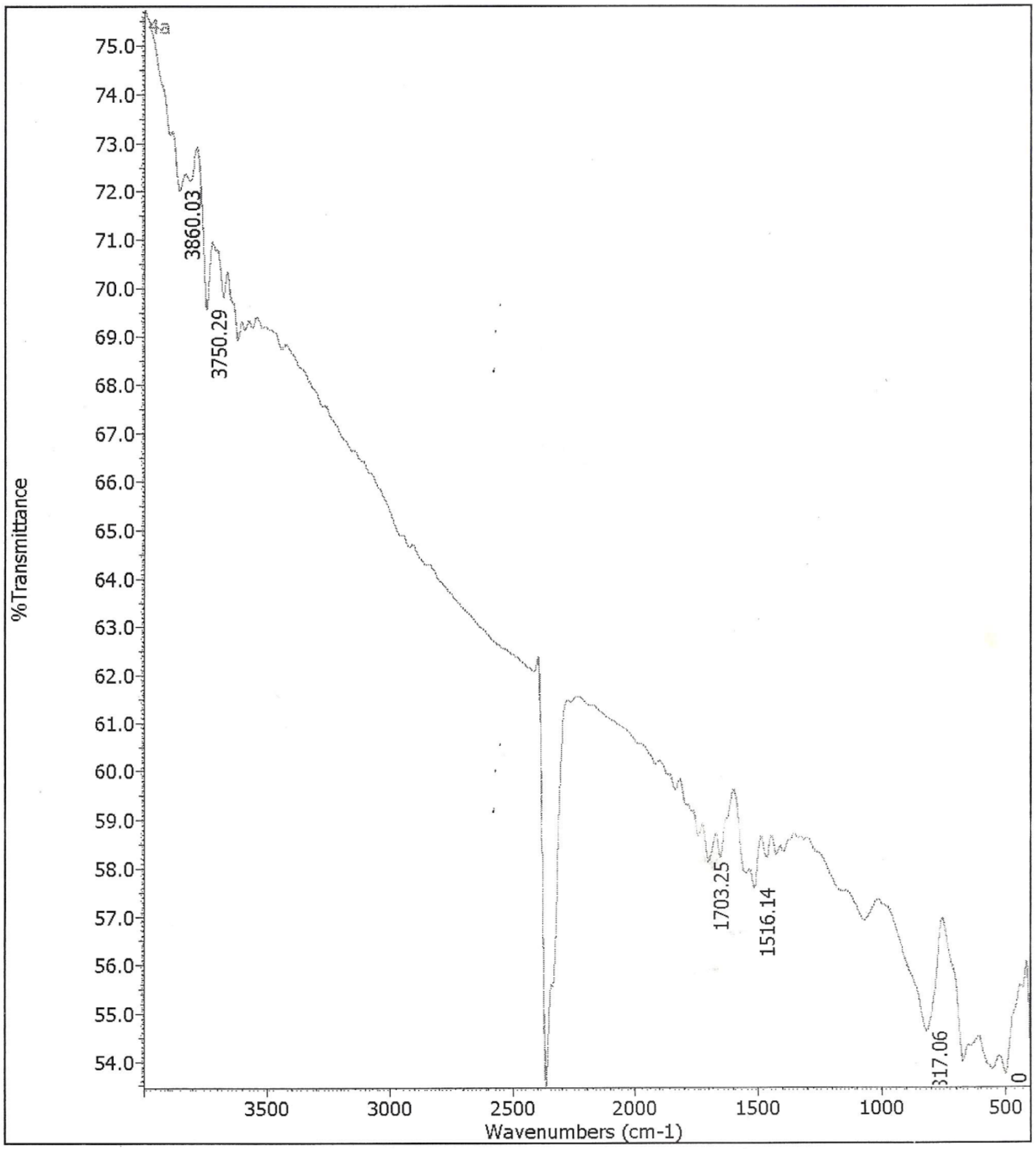


Figure A1: Infrared spectral of dye intermediate 4a, 1-amino-2-hydroxy-4- methyl-5-cyano-6-pyridone

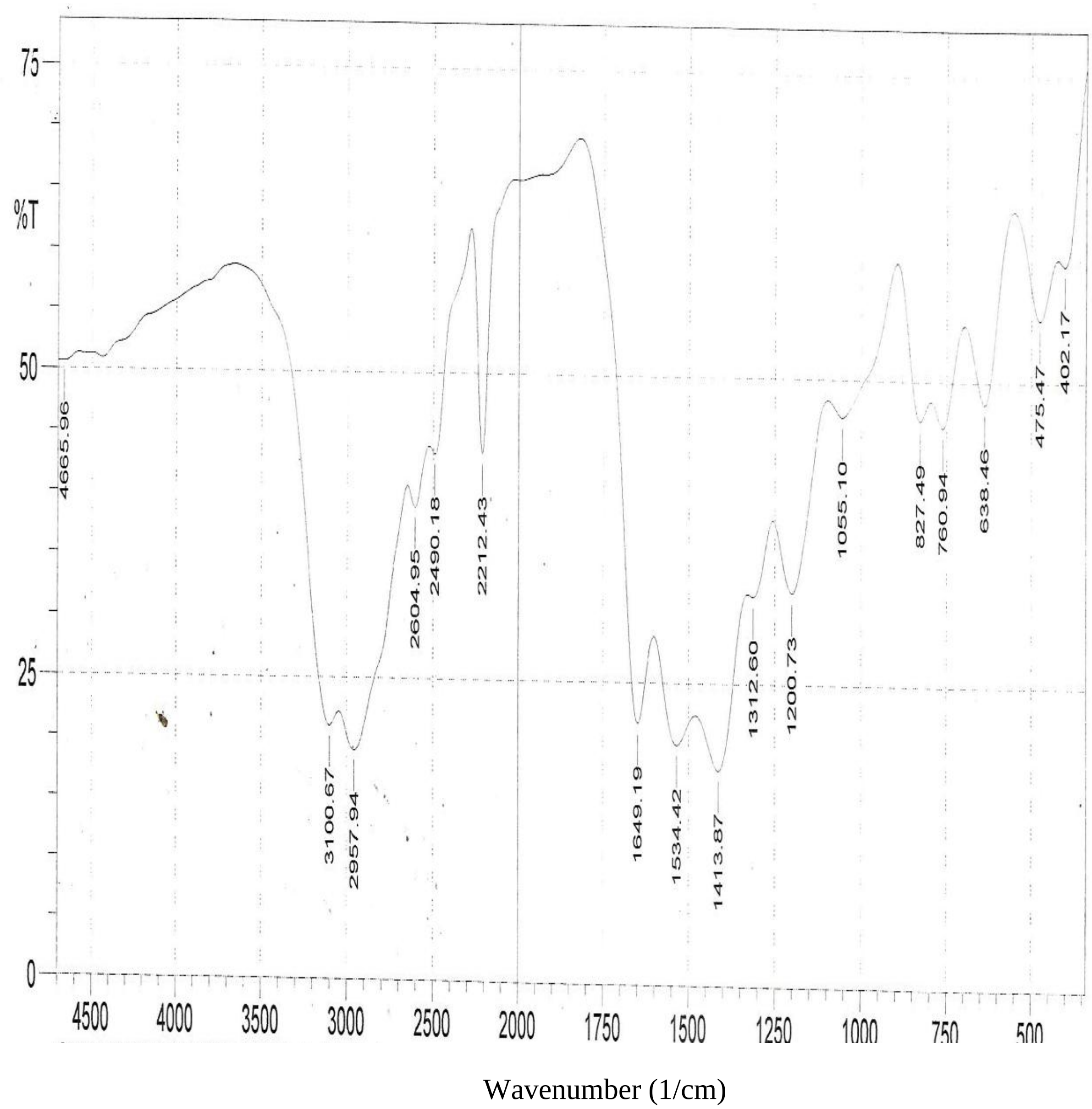
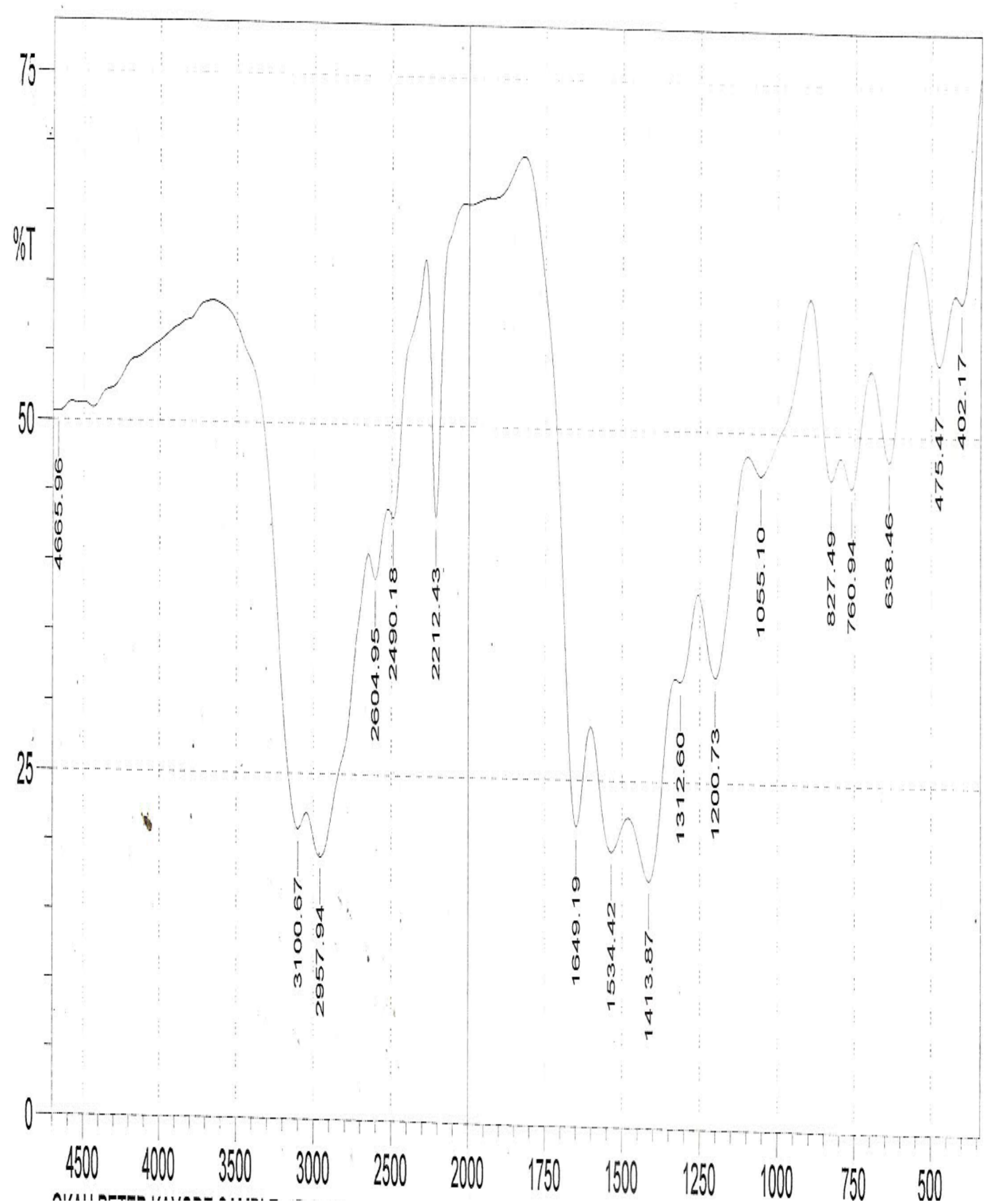
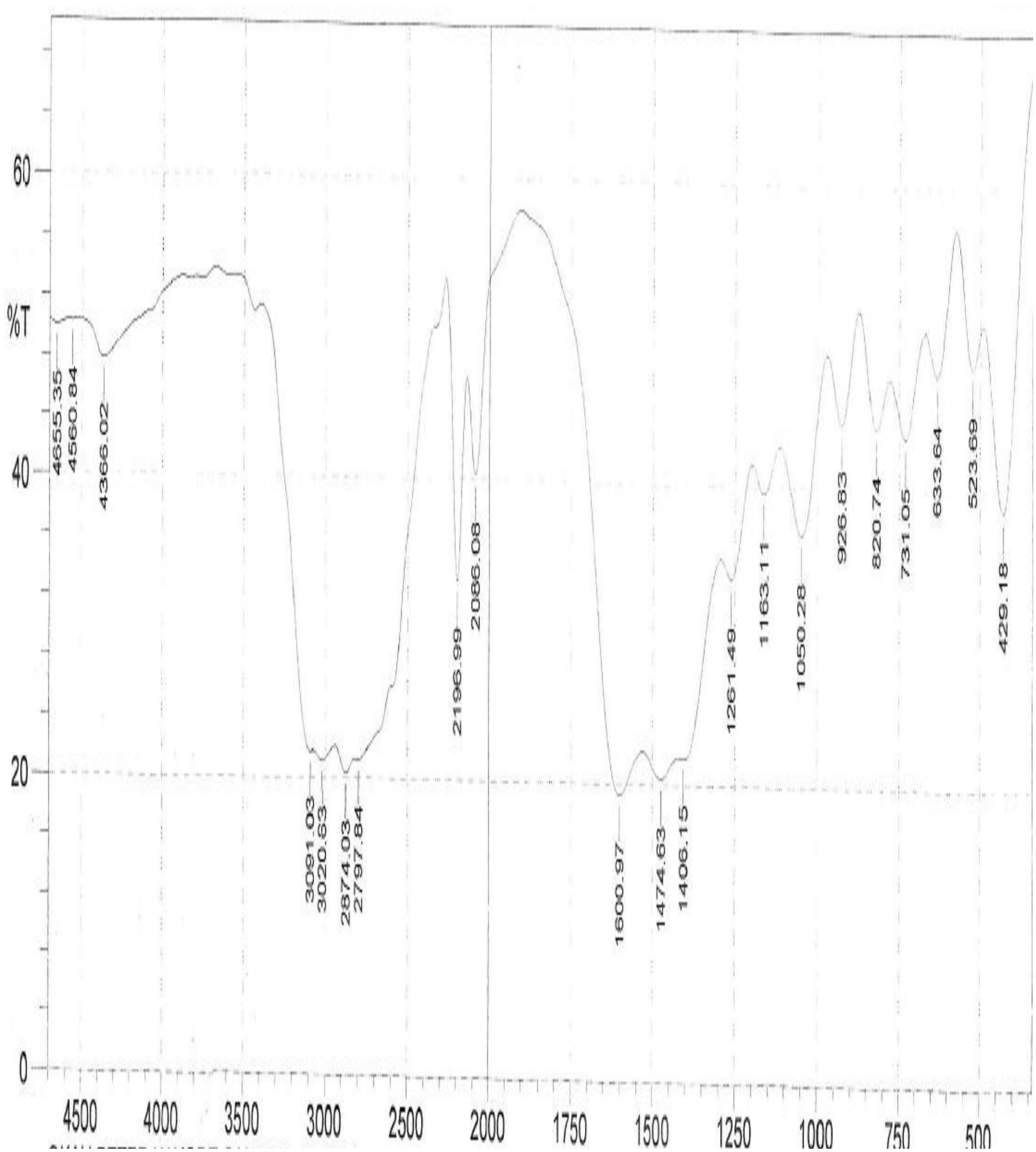


Figure A2: Infrared spectrum of dye intermediate 4b, 1-methyl-2-hydroxy-4- methyl-5-cyano-6-pyridone



Wavenumber (1/cm)

Figure A3: Infrared spectrum of dye intermediate 4c, 1-ethyl-2-hydroxy-4- methyl-5-cyano-6-yridone



Wavenumber (1/cm)

Figure: A4 Infrared spectrum of dye intermediate 4d, 1-butyl-2-hydroxy-4- methyl-5-cyano-6-yridone

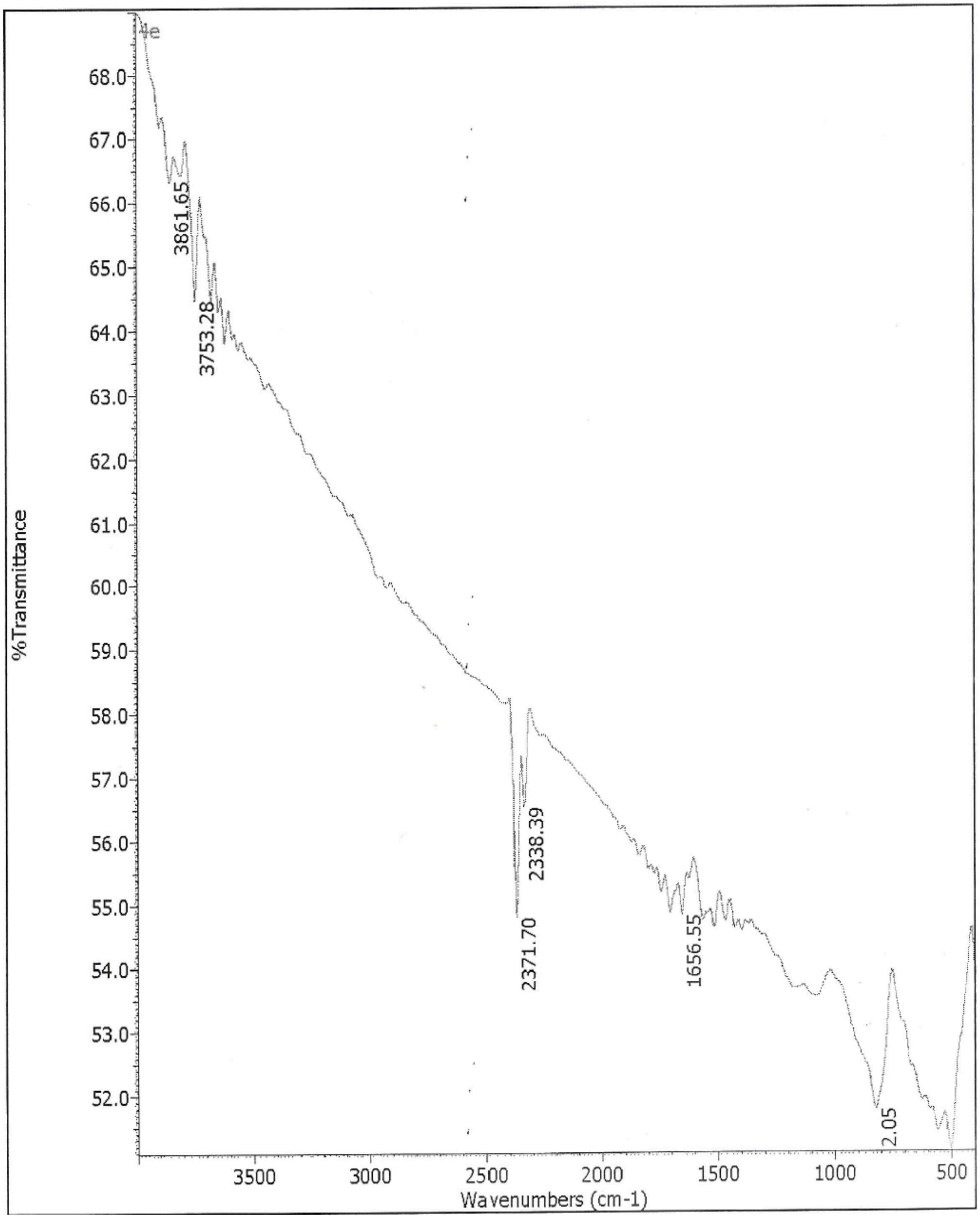
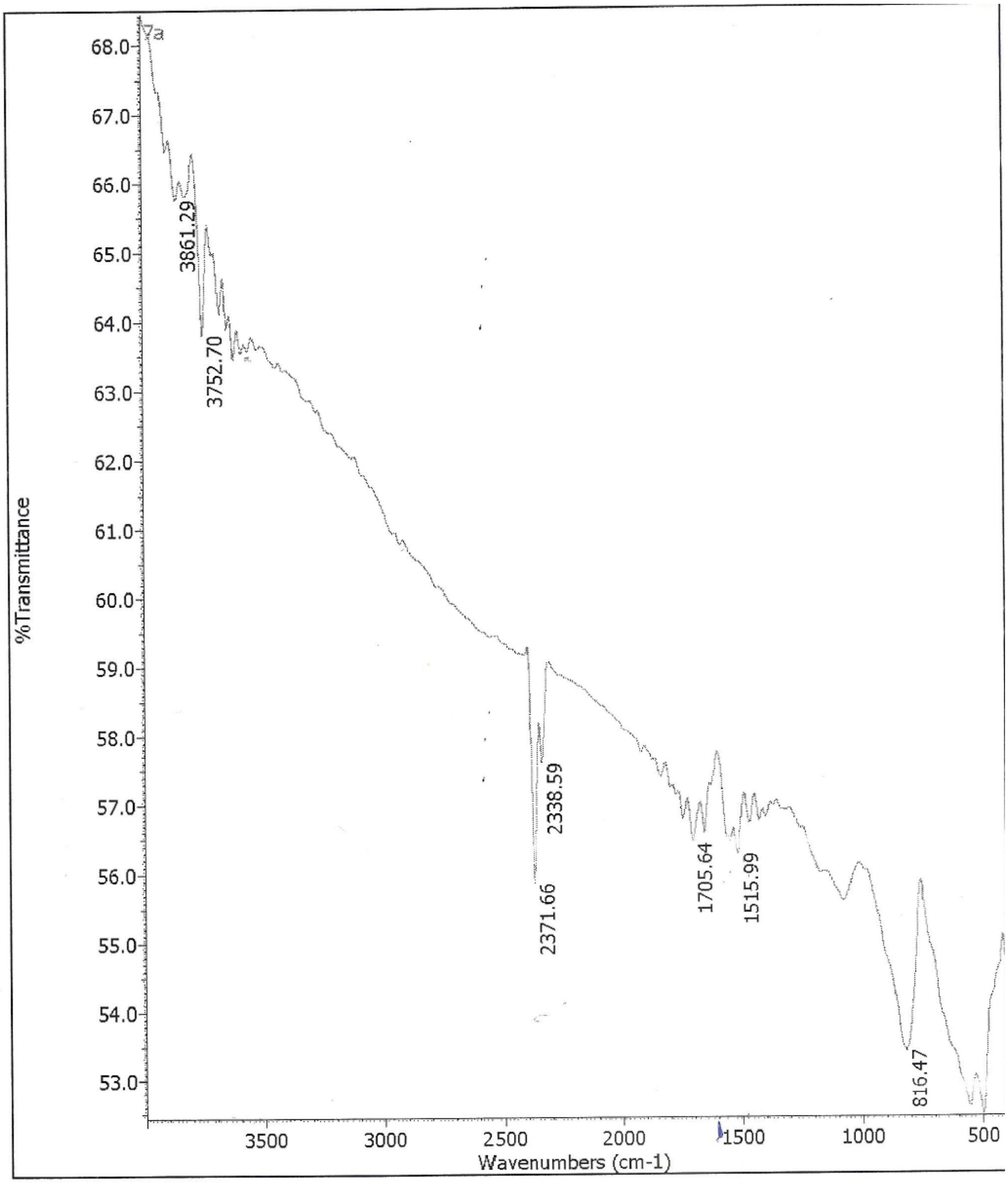


Figure A5: Infrared spectrum of dye intermediate 4e, 1-dodecyl-2-hydroxy-4- methyl-5-cyano-6-yridone

APPENDIX B: FTIR SPECTRAL FOR DYES



Appendix B1: Infrared spectrum of dye 7a

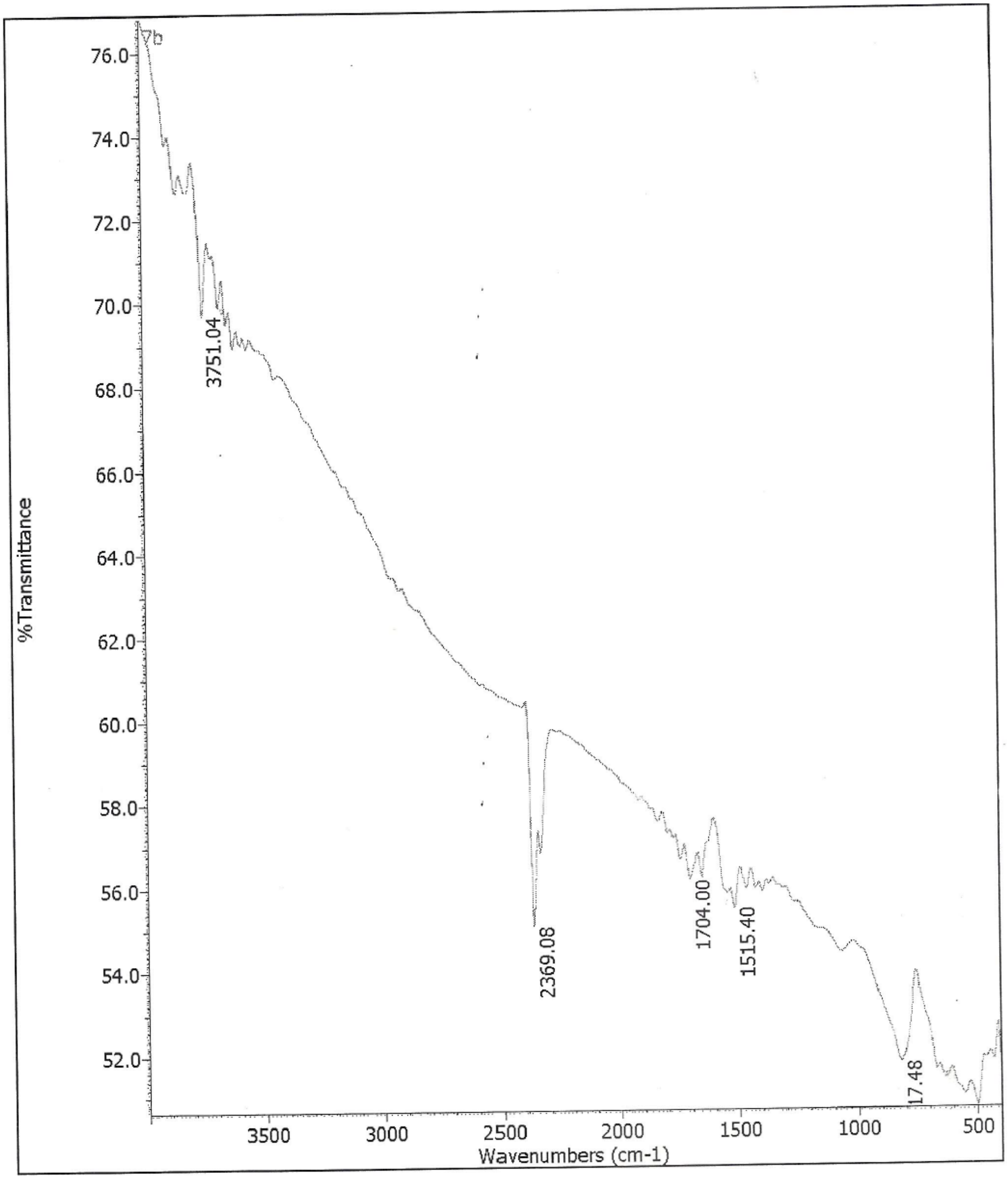


Figure B2: Infrared spectrum of dye 7b

Figure B3: Infrared spectrum of dye 7c

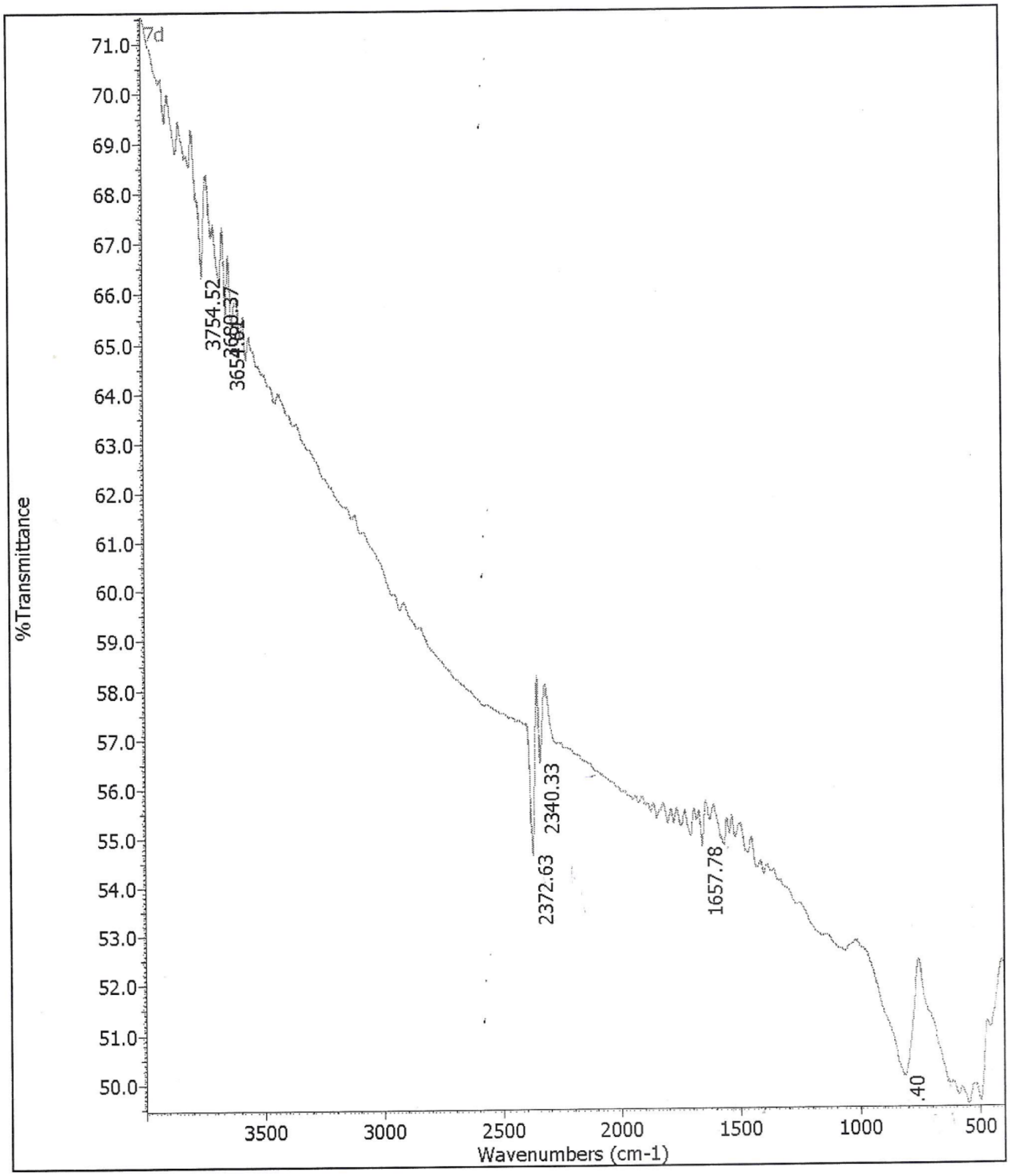


Figure B4: Infrared spectrum of dye 7d

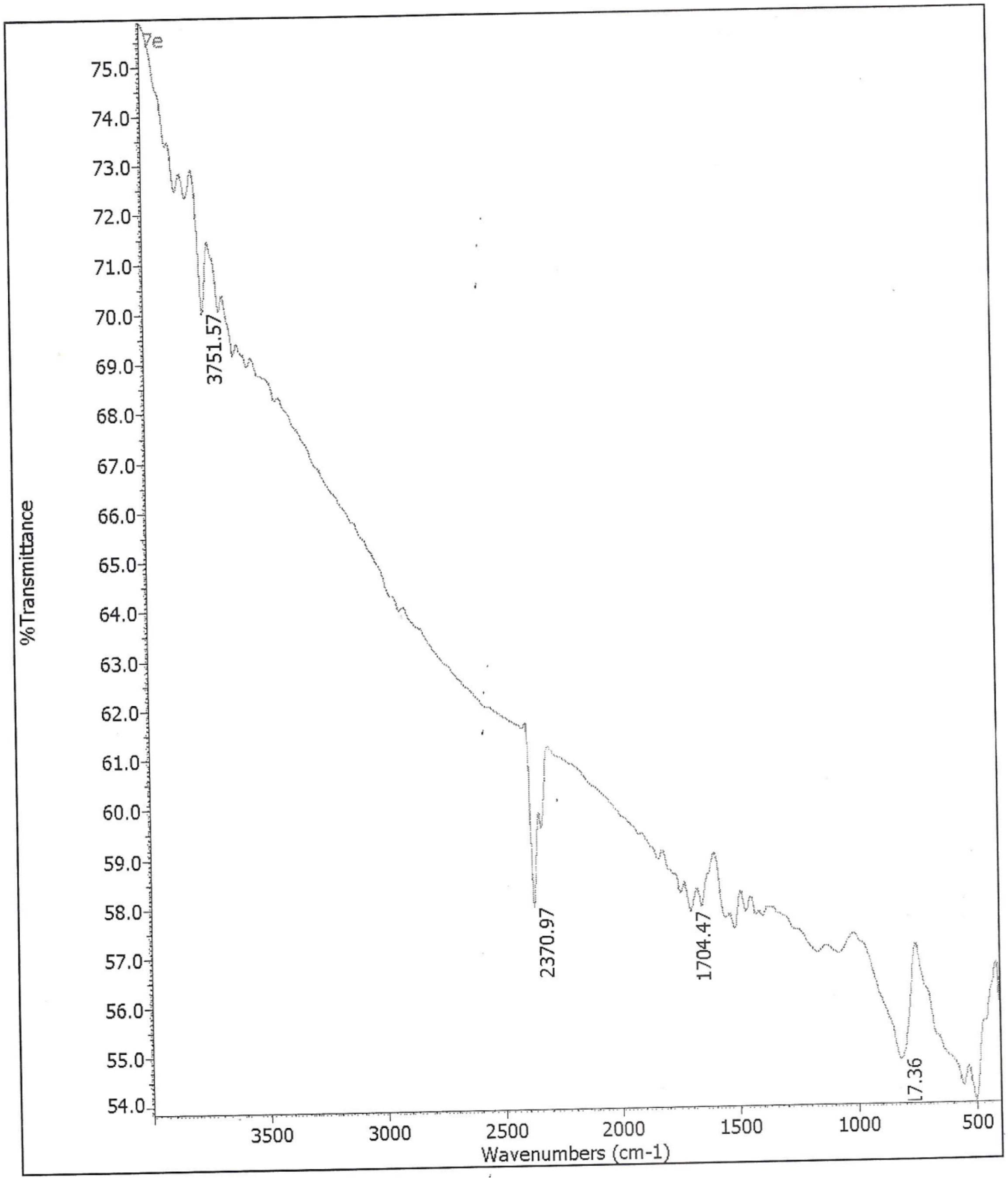


Figure B5: Infrared spectrum of dye 7e

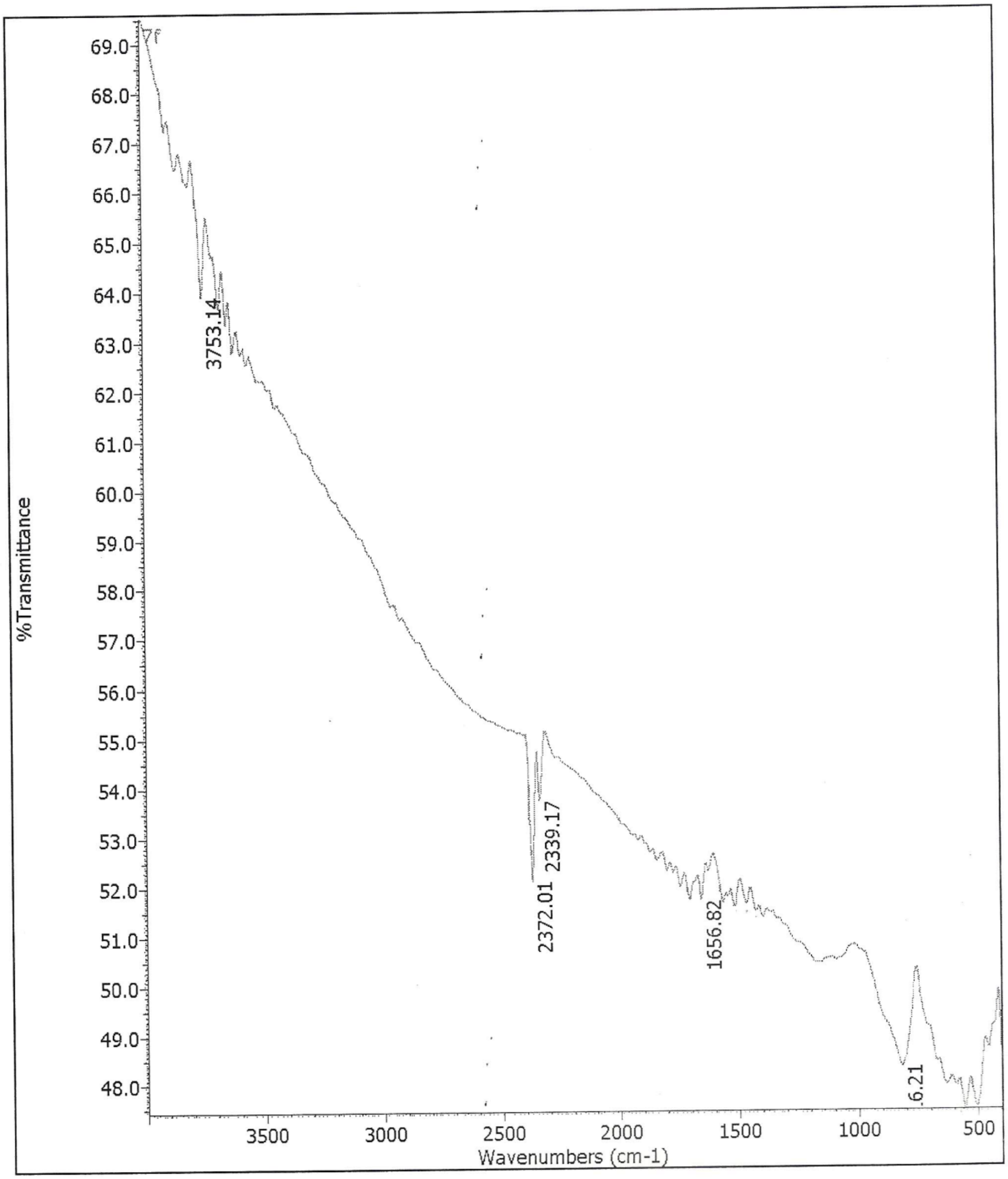


Figure B6: Infrared spectrum of dye 7f

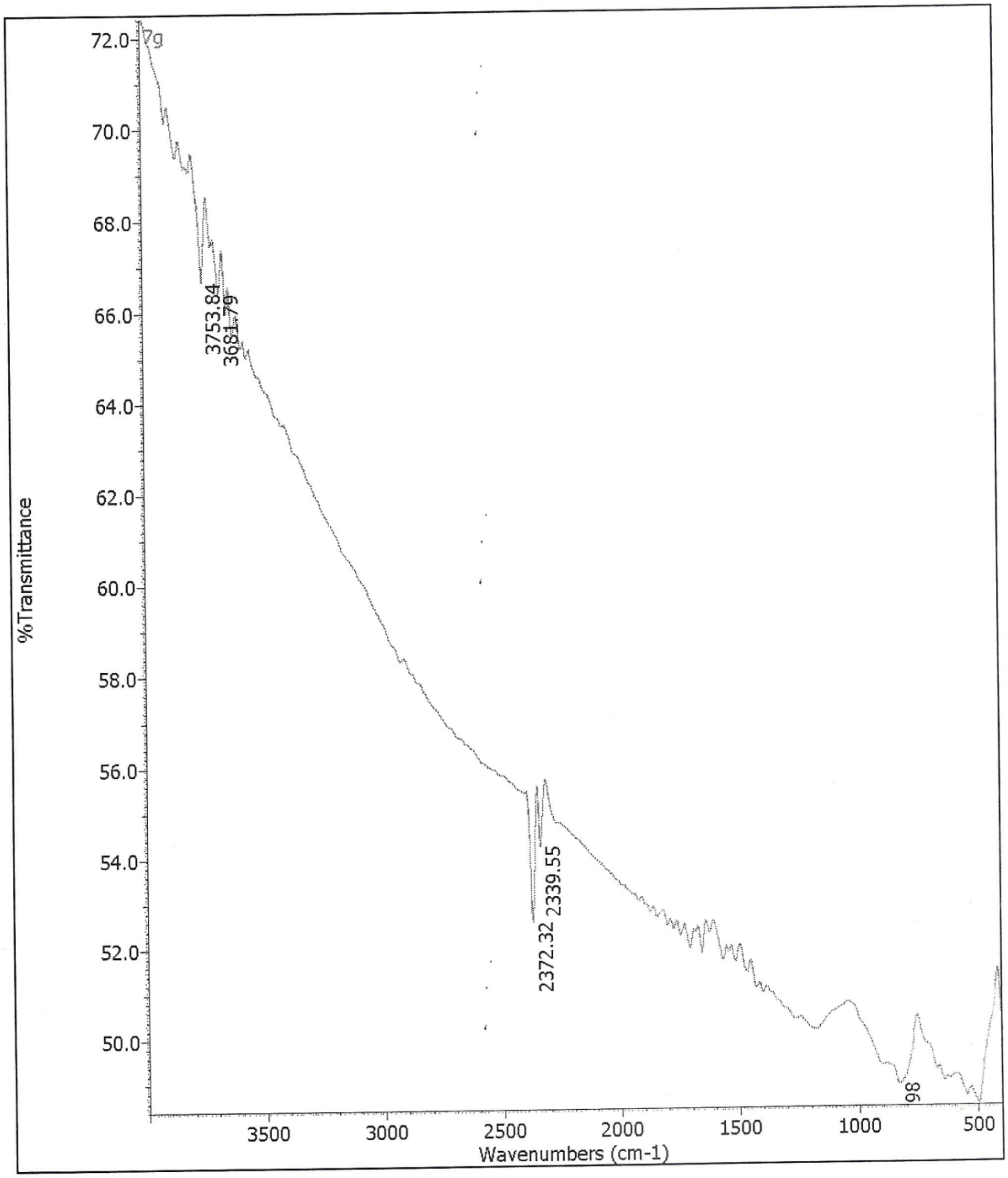


Figure B7: Infrared spectrum of dye 7g

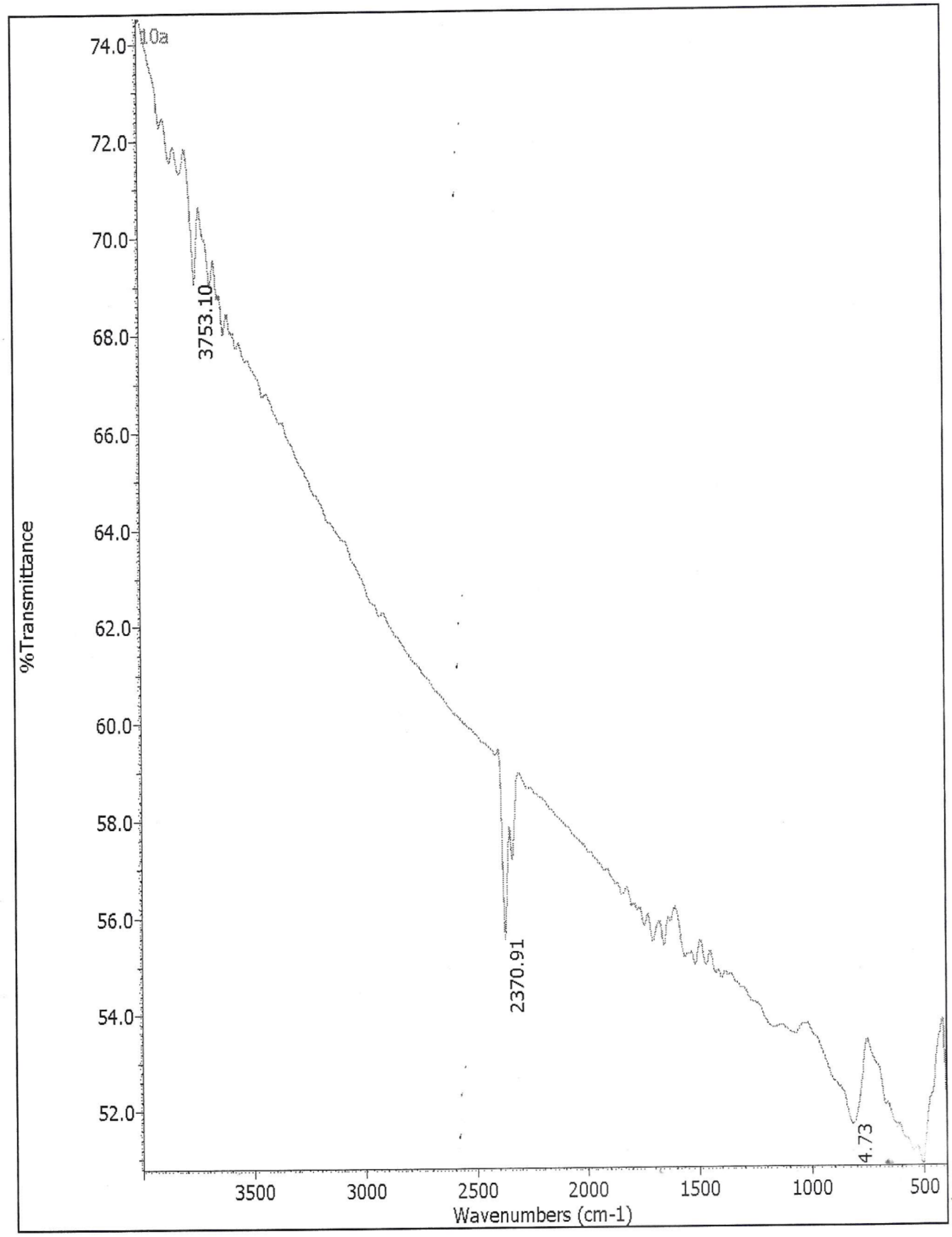


Figure B8: Infrared spectrum of dye 10a

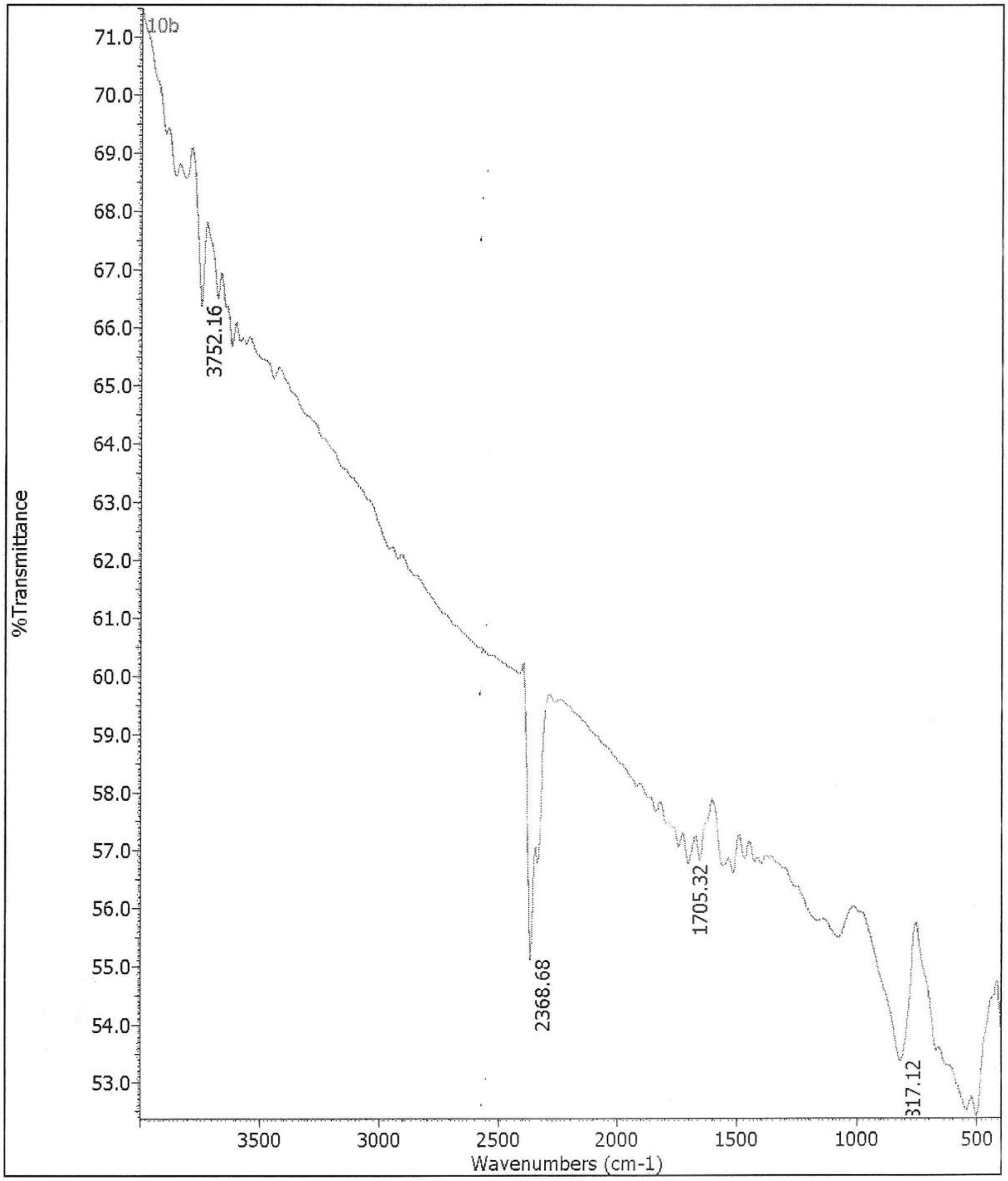


Figure B9: Infrared spectrum of dye 10b

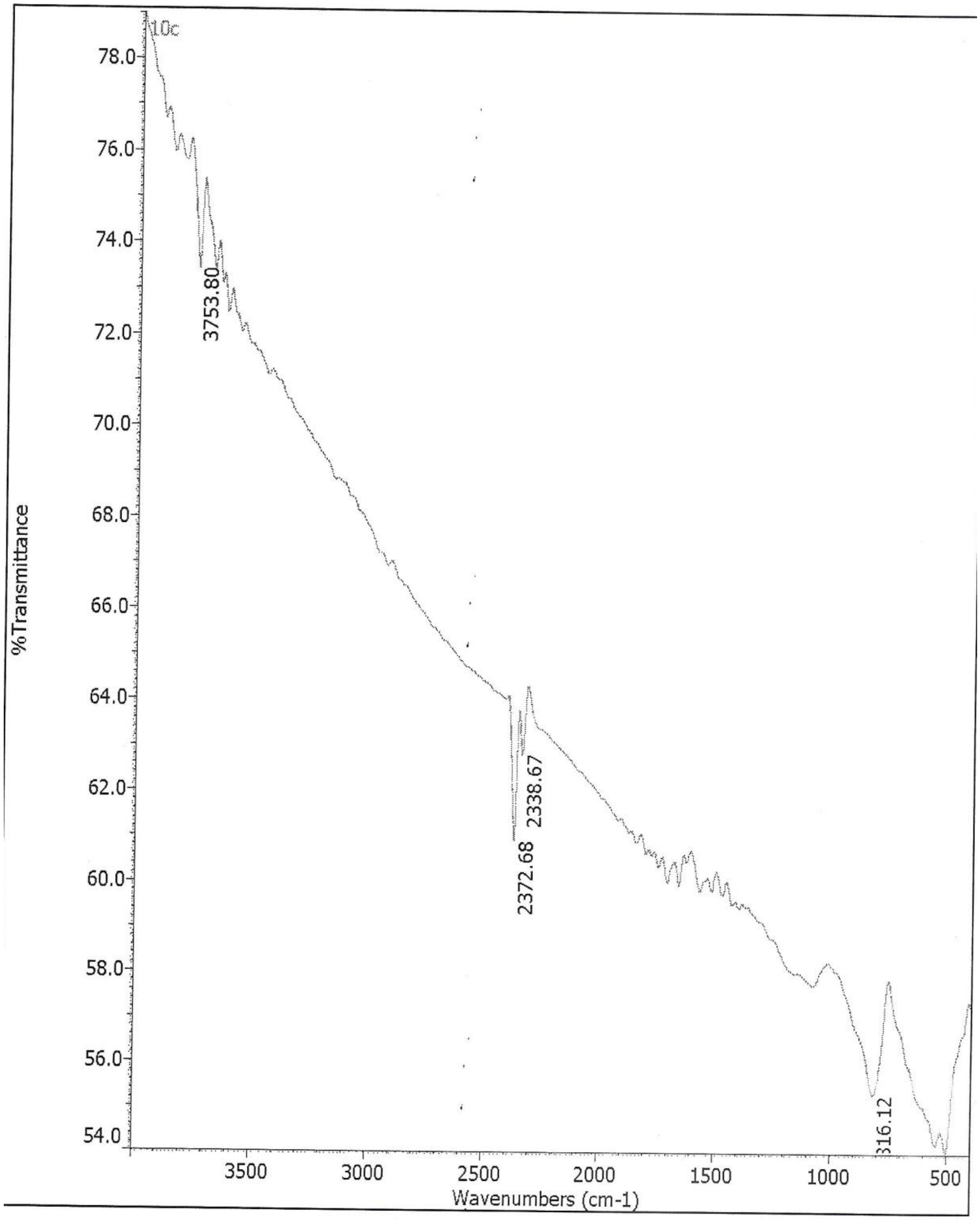


Figure B10: Infrared spectrum of dye 10c

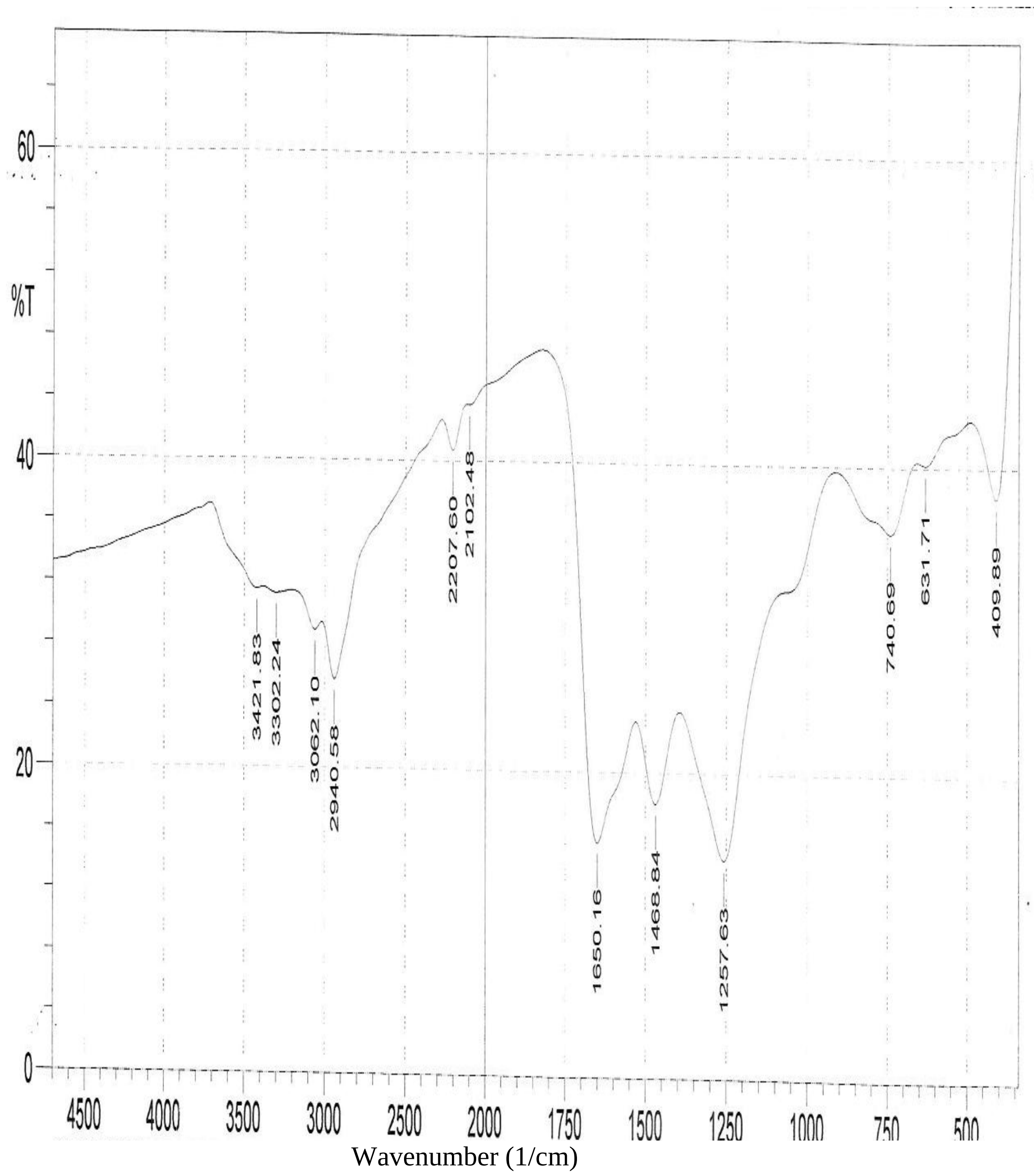


Figure B11: Infrared spectrum of dye 10d

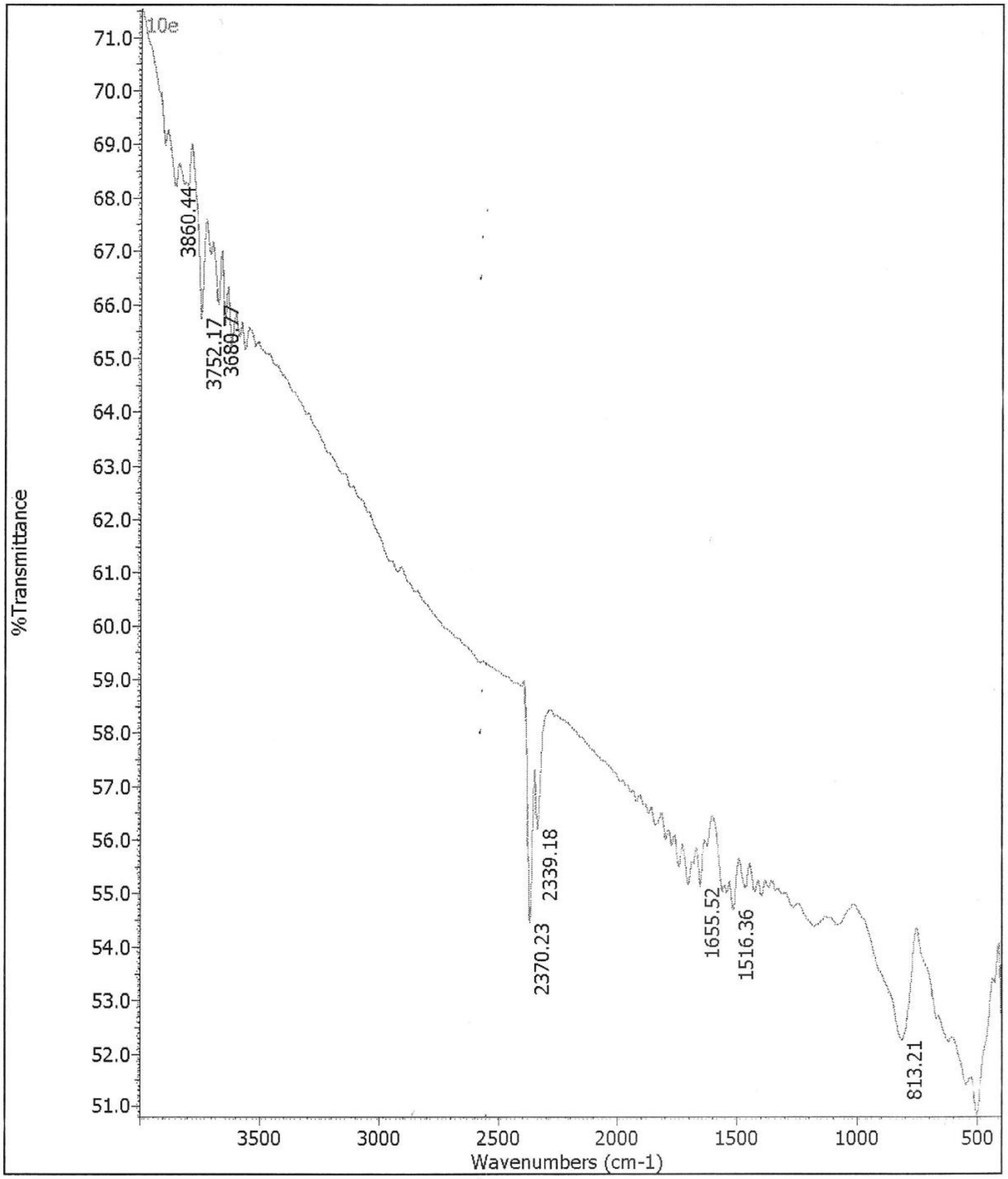


Figure B12: Infrared spectrum of dye 10e

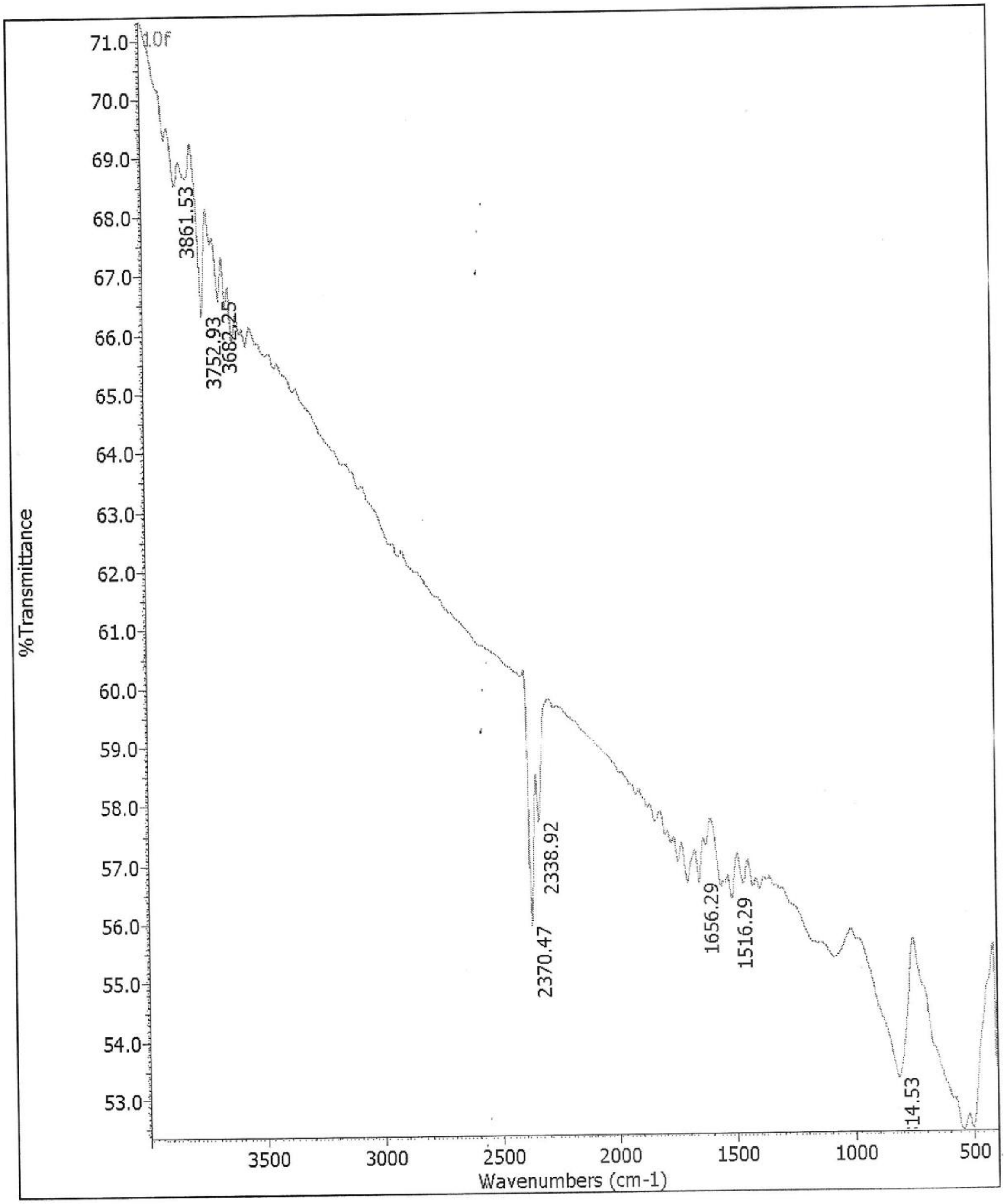


Figure B13: Infrared spectrum of dye 10f

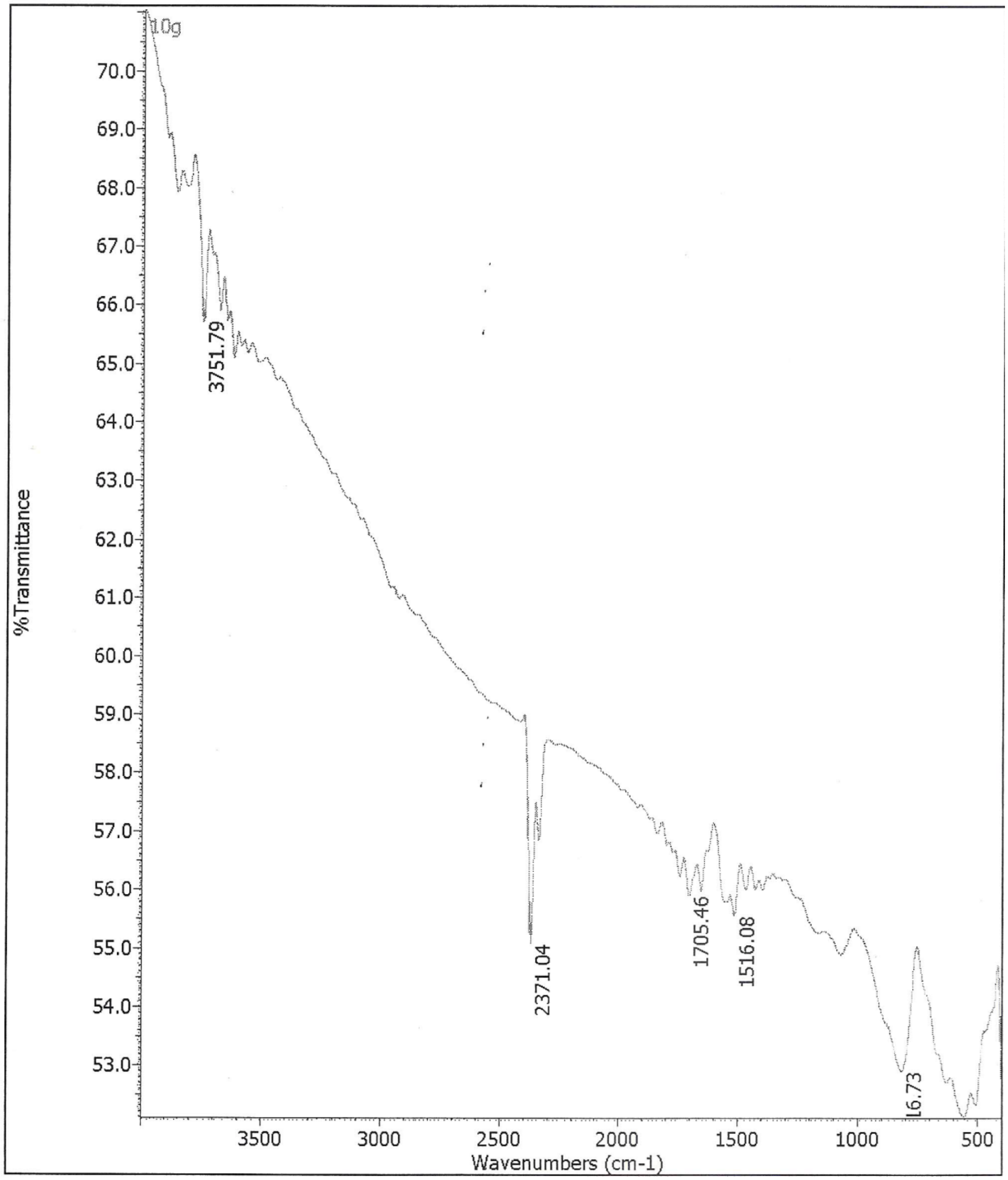


Figure B14: Infrared spectrum of dye 10g

Appendix C: Effect of Temperature, Time and pH on Dye Exhaustion

Table C1: Effect of temperature on dyeing exhaustion for monoazo dyes (7a – 7e)

Temperature (^{O}C)	7a	7b	7c	7d	7e
0	0	0	0	0	0
20	47.29	43.43	25.93	42.45	22.45
40	58.8	65.62	67.27	50.46	33.31
60	88.07	71.5	83.33	62.32	45.68
80	92.68	76.16	87.22	78.6	52.12
100	95.25	91.86	90.34	82.1	66.75

Table C2: Effect of temperature on dyeing exhaustion for disazo dyes (10a – 10e)

Temperature (^{o}C)	10a	10b	10c	10d	10e
0	0	0	0	0	0
20	30.82	28.12	28.98	15.74	28.06
40	46.2	37	46.12	26.76	35.63
60	65.4	53.13	48.21	33.21	44.1
80	70.12	63.43	52.12	42.98	47.14
100	79.88	75.31	61.07	52.28	50.33

Table C3: Effect of time on dye exhaustion for monoazo dyes (7a – 7e)

Time (min)	7a	7b	7c	7d	7e
0	0	0	0	0	0
20	59.62	60.41	69.67	42.81	38.64
40	71.79	90.59	79.55	55.51	52.34
60	95.25	91.86	87.22	66.09	60
80	96.25	94.23	92.38	81.81	75.34
100	96.61	94.59	92.43	87.56	75.56

Table C4: Effect of time on dye exhaustion for disazo dyes (10a – 10e)

Time (min)	**10a**	**10b**	**10c**	**10d**	**10e**
0	0	0	0	0	0
20	37.55	49.69	48.21	12.17	41.43
40	49.18	59.69	53.93	33.23	45.07
60	79.88	75.31	61.07	52.28	50.33
80	87.5	75.94	68.93	69.15	54.34
100	88.62	78.13	70	72.45	56.17

Table C5: Effect of pH on dye exhaustion for monoazo dyes (7a – 7e)

pH	7a	7b	7c	7d	7e
4	60.98	75.2	62.78	66.23	58.54
5	98.24	96.64	98.45	94.63	94.05
6	85.76	82.85	75.06	84.89	78.42
7	85.65	82.8	75.1	84.88	78.4

Table C6: Effect of pH on dye exhaustion for disazo dyes (10a – 10e)

pH	10a	10b	10c	10d	10e
4	64.08	67.29	58.67	48.69	48.88
5	95.78	90.26	87.9	85.98	92.05
6	83.29	80.17	69.7	62.89	70.56
7	82.25	80.05	69.2	62.76	70.6

Appendix D: Dyed Polylactide Fabrics with Disperse Dyes

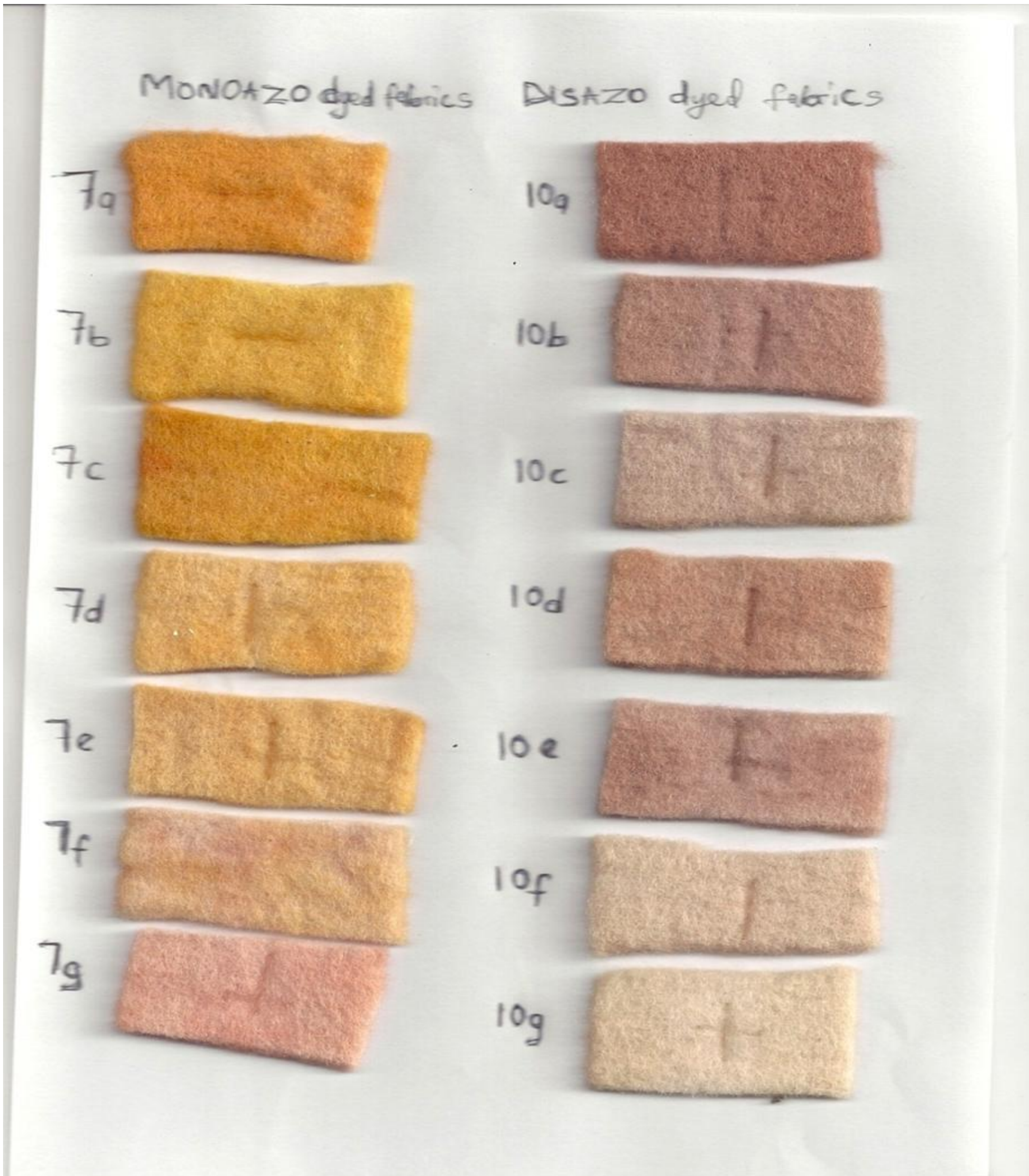


Plate D1: Fabrics dyed with synthesized monoazo and disazo disperse dyes