SYNTHESIS, APPLICATION AND ANTIMICROBIAL PROPERTIES OF AZO DYES DERIVED FROM 2-AMINOTHIOPHENE AND CONVENTIONAL AMINES AS DIAZO COMPONENTS

BY

OSAZEE BRIGHT AGHO

DEPARTMENT OF POLYMER AND TEXTILE SCIENCE,

AHMADU BELLO UNIVERSITY,

ZARIA, NIGERIA

JULY, 2017

SYNTHESIS, APPLICATION AND ANTIMICROBIAL PROPERTIES OF AZO DYES DERIVED FROM 2-AMINOTHIOPHENE AND CONVENTIONAL AMINES AS DIAZO COMPONENTS

BY

OSAZEE BRIGHT AGHO

PGD Analytical Chemistry, A.B.U. (Zaria) 2013

(P14SCTX8021)

A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE (M.Sc.) IN COLOUR CHEMISTRY AND TECHNOLOGY

DEPARTMENT OF POLYMER AND TEXTILE SCIENCE,

FACULTY OF PHYSICAL SCIENCES,

AHMADU BELLO UNIVERSITY,

ZARIA, NIGERIA

JULY, 2017

DECLARATION

I, declare that the work in this Dissertation entitled "SYNTHESIS, APPLICATION AND ANTIMICROBIAL PROPERTIES OF AZO DYES DERIVED FROM 2-AMINOTHIOPHENE AND CONVENTIONAL AMINES AS DIAZO COMPONENTS" has been carried out by me in the Department of Polymer and Textile Science. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this Dissertation was previously presented for another degree or diploma at this or any other Institution.

_____	_____
Osazee Bright AGHO	Date
Name of student	

CERTIFICATION

This project dissertation entitled ‘‘SYNTHESIS, APPLICATION AND ANTIMICROBIAL PROPERTIES OF AZO DYES DERIVED FROM 2-AMINOTHIOPHENE AND CONVENTIONAL AMINES AS DIAZO COMPONENTS” by Osazee Bright AGHO meets the regulations governing the award 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.

_____ _____

Prof. P.O. NKEONYE Date
Chairman, Supervisory Committee

_____ _____

Dr. A.A. KOGO Date
Member, Supervisory Committee

_____ _____

Prof. A.S. LAWAL Date
Head of Department

_____ _____

Prof. S.Z. ABUBAKAR Date
Dean, School of Postgraduate Studies

DEDICATION

This dissertation is dedicated to the Almighty God for His Infinite Mercy, Protection, Divine Guidance, Inexhaustible Love, Provision, Grace and Strength granted to me throughout my course of study.

ACKNOWLEDGEMENT

My heartfelt gratitude goes to a number of people who had contributed so much to the success of my academic year in this institution. First of all, my sincere gratitude, deep appreciation and unquantified thanks to Prof. P.O. Nkeonye for his invaluable guidance, assistance, close and meticulous supervision, constructive criticism, moderation, correction and patience which saw me through to the successful completion of this research.

I am equally grateful to Prof K.A Bello and Dr. A.A Kogo for their support, guidance and understanding throughout the research work. My sincere appreciation goes to the academic and the non-academic staff of Polymer and Textile Science Department of Ahmadu Bello University, Zaria.

My profound gratitude and love goes out to my impeccable and adorable Mother Mrs. Roseline Agho and Mother In-law Mrs. Theresa Angulu for their love and support. I also remain grateful to my siblings Senator Frank Agho, Sylvia Agho, Osarodion Agho, and Joy Agho.

My profound gratitude and love also go to my dearest wife Patience and our adorable son Abraham Osazee Bright for their *adinfinitum* support and encouragement.

I wish to express my sincere gratitude to Dr. I.K Adamu (DG/CEO, NILEST), Dr. E.N. Oparah, Dr. P.H. Bukar, Mr. A. Okele, Mr. Daniel, Mr. J.Z. Jakada, Mr. A Kutman, Mr. Paschal Mr. Jerry Akawu, Mr. Obadahun Joshua, Mr. Collins E. Mr. Ibrahim Y. Magaji, staff of HND Chemistry for their continuous encouragement and support during the course of this work, may helpers of destiny be littered across your path. I wish to specially thank and appreciate my course mates, staff and students of Department of Science Laboratory Technology, Nigerian Institute of Leather and Science Technology (NILEST) for their understanding. I say a big thank you and may God bless you all.

ABSTRACT

Twelve different monoazo heterocyclic disperse and acid dyes of low molecular weight derived from 2-aminothiophene and conventional amines as diazo components were successfully synthesized. The identities of the synthesized dyes and intermediates were investigated using spectroscopic analysis such as Uv-visible spectrometry, Fourier Transform Infrared Spectrometry and Gas Chromatography Mass Spectrometry. The 2-aminothiophene intermediates and heterocyclic disperse dyes were synthesized using the Gewald's method and the molar mass of the synthesized intermediates were between 257-285 g/mol while that of the synthesized dyes were between 305-614 g/mol. All the synthesized dyes absorbed within the visible region of the electromagnetic spectrum but the heterocyclic disperse dyes synthesized from the 2-aminothiophene intermediates were more bathochromic than those of the conventional amines dyes. The heterocyclic disperse dyes gave good exhaustion ranging from 60 % to 78 % on polyester fabric while the acid dyes on chrome tanned leather gave an excellent exhaustion of 80 % to 87 %. The dyes gave mostly brown, deep purple and orange shades and exhibited good to excellent fastness properties on the dyed substrates. For wash fastness, it was between 5 (excellent) and 3 (good), while for light fastness it was between 6 (good) and 4 (moderate). The antimicrobial screening of the synthesized dyes against six (6) different microorganisms were assessed using the Agar Well diffusion method and the results showed zones of inhibition ranging from 3-34 mm, Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal/Fungicidal Concentration (MBC/MFC) values as low as 12.5 mg/ml, which indicate that the dyes can be effective against infectious diseases which these microorganisms can cause.

TABLE OF CONTENTS

TITLE PAGE..……...……i

DECLARATION ii

CERTIFICATION iii

DEDICATION.....iv

ACKNOLEDGEMENT.....v

ABSTRACT.....vi

TABLE OF CONTENTS……vii

LIST OF TABLES ...……vii

LIST OF FIGURES ....……xii

LIST OF SCHEME……... xiii

LIST OF APPENDICES ……..……..xiv

CHAPTER ONE 1

1.0 INTRODUCTION 1

1.1 Azo Dyes ……...1

1.1.1 Disperse Dyes ……3

1.1.2 Acid Dyes ……..3

1.2 Statement of the Research Problem ……...3

1.3 Justification ……...4

1.4 Aim and Objectives of the study ……...4

CHAPTER TWO ……...6

2.0 LITERATURE REVIEW ……..6

2.1 Development of Synthetic Dyes ……..……6

2.1.1 Basic dyes ……9

2.1.2 Vat dyes (Indigoid) ……10

2.1.2.1 Anthraquinone vat dyes ……...11

2.1.2.2 Solubilised vat dyes ……11

2.1.3 Sulphur dyes ……...11

2.1.4 Direct dyes ……..12

2.1.5 Phthalocyanine dye ……13

2.1.6 Azoic dyes ……..13

2.1.7 Acid dyes ……14

2.1.8 Metal Complex dyes ……...15
2.1.9 Disperse dyes ……..15
2.1.10 Reactive dyes ……...17
2.2 Azo dye synthesis ……..18
2.3 Heterocyclic Disperse Dyes ……..21
2.4 Fibre Structure in Relation to Dyeing ……...22
2.5 Dyes and their Required Properties ……...23
2.6 Forces of Attraction between Dye and Fibres during Dyeing ……...23
2.6.1 Ionic Bonds (Ionic Forces) ……24
2.6.2 Hydrogen Bonding ……24
2.6.3 Covalent Bonding ……...25
2.6.4 Van der Waals Forces ……25
2.7 Hides and skins ……..26
2.7.1 Functions of Hides and Skins ……26
2.7.2 Tanning ……...26
2.7.3 Tanning Procedure ……27
2.7.3.1 Vegetable tanning ……....28
2.7.3.2 Mineral tannin (chrome tanning) ……28
2.7.4 Dyestuffs Available for the leather Industries ……29
2.7.5 Dyeing of Leather ……...29
2.7.6 Dye selection for leather application ……..30
2.8 Polyester Fibre ……...30
2.9 Dyes for polyesters ……31
2.10 Antimicrobial Dyes ……31
CHAPTER THREE ……34
3.0 MATERIALS AND METHODS ……34
3.1 Materials ……34
3.2 Apparatus and Equipment ……34
3.3 Synthesis of Aminothiophene Intermediates ……34
3.3.1 Aminothiophene intermediate 1 ……34
3.3.2 Aminothiophene intermediate 2 ……35
3.4 Purification and Determination of some Physical properties of the Synthesized 2-Aminothiophene Intermediates ……...35
3.5 Procedure for Diazotization and Coupling ……35

3.5.1 Diazotization of Intermediates 1 And 2 ……35
3.5.2 Diazotization of Intermediate 3 ……..36
3.5.3 Diazotization of Intermediate 4 ……..36
3.5.4 Coupling Reaction ……..36
3.6 Purification of the Dyes ……37
3.7 Percentage Yield of Dyes and Intermediates ……37
3.8 Characterization of the Synthesized Dyes and Intermediates ……...37
3.8.1 Melting Point Determination ……..38
3.8.2 Molar Extinction Coefficient ……38
3.8.3 Determination of Visible Absorption Spectra ……38
3.8.4 FT-IR Determination ……..39
3.8.5 Gas Chromatography-Mass Spectrometry (GC-MS) ……39
3.9 Application of Dyes ……..39
3.9.1 Dyeing of polyester ……39
3.9.2 Dyeing of leather ……40
3.10 Determination of Dyebath Exhaustion ……41
3.11 Assessment of Fastness Properties ……..41
3.11.1 Wash Fastness Test ……..41
3.11.2 Light Fastness Test ……...42
3.12 Evaluation of the Antimicrobial Activity of Azo Dyes ……...42
3.12.1 Test organisms ……42
3.12.2 Culture media ……...42
3.12.3 Determination of inhibitory activity (sensitivity test) of the synthesized dyes using Agar well diffusion method ……43
3.12.4 Determination of minimum inhibitory concentration (MIC) ……..43
3.12.5 Determination of minimum Bactericidal/fungicidal concentration (MBC/MFC) …..44
CHAPTER FOUR ……...45
4.0 RESULTS ……45
4.1 Synthesis of 2-Aminothiophene Intermediates ……...45
4.1.1 Synthetic Route for the 2-Aminothiophene Intermediates ……..45
4.1.2 Physical Properties of 2-aminothiophene Intermediates ……45
4.2 Synthesis of the Azo Dyes ……..46
4.2.1 Synthetic route for the Synthesis of the Azo Dyes ……..46
4.2.2 Physical Properties of the Synthesized Azo Dyes ……...51

4.3 Characterization of the Synthesized Intermediates and Dyes ……51
4.3.1 Visible absorption Spectroscopy of Dyes ……...51
4.3.2 Infra-Red Spectra of the Intermediates and Dyes ……...51
4.3.3 GC-MS of the Intermediates and Dyes ……...51
4.4 Antimicrobial Activity of the Synthesized Dyes ……51
4.5 Dyeing of Polyester Fabric and Chrome Tanned Leather ……...52
4.5.1 Dyeing Exhaustion of the Synthesized Dyes ……..52
4.5.2 Assessment of Fastness Properties to Washing and Light ……..52
4.5.2.1 Wash fastness ……..52
4.5.2.2: Light Fastness of the using 8 Blue Wool Standard ……52
CHAPTER FIVE ……64
5.0 DISCUSSION ……64
5.1 Synthesis and Physical Properties of 2-aminothiophene Intermediate ……...64
5.2 Synthesis and Physical Properties of the Azo Dyes ……65
5.3 Characterization of the Synthesized Intermediates and Dyes ……....66
5.3.1 Visible absorption spectroscopy of dyes in DMSO and Methanol ……66
5.3.2 The Infra-Red Spectra of the Intermediates and Dyes ……69
5.3.3 GC-MS Spectra of the Synthesized Intermediates and Dyes ……..69
5.4 Antimicrobial Screening of the Synthesized Dyes ……..70
5.5 Dyeing of Polyester Fabric and Chrome Tanned Leather ……...72
5.5.1 Dye Exhaustion on Polyester Fibre and Chrome Tanned Leather ……..72
5.5.2 Wash Fastness of the Synthesized Dyes on Polyester Fibre and Chrome Tanned Leather using ISO 3 Standard ……73
5.5.3 Light Fastness of the Synthesized Dyes on Polyester Fibre and Chrome Tanned Leather using 8 Blue Wool Standards ……74
CHAPTER SIX ……...75
6.0 SUMMARY, CONCLUSION AND RECOMMENDATION ……...75
6.1 Summary ……75
6.2 Conclusion ……...77
6.3 Recommendations ……...77
CONTRIBUTION TO KNOWLEDGE ……..78
REFERENCES ……79

LIST OF TABLES

Table	Title	Page
4.1:	Physical Properties of 2-aminothiophene Intermediates……..53	
4.2:	Physical Properties of the synthesized azo dye…….....54	
4.3:	Visible absorption Spectroscopy of Dyes…….…….……..55	
4.4:	The Infra-Red Spectra of the Intermediates and Dyes…….…….....56	
4.5:	GC-MS Fragments of Intermediates and Dyes……...…….57	
4.6:	Zone of Inhibition (mm) of the Test Organisms by the Synthesized Dyes ……..…...58	
4.7:	Minimum Inhibitory Concentration (MIC) mg/ml of the Synthesized Dyes against Test Microorganisms …….…….....……59	
4.8:	Minimum Bactericidal/Fungicidal Concentration (MBC/MFC) mg/ml of the Synthesized Dyes against Test Microorganisms……...……...60	
4.9:	Dye Exhaustion on Polyester Fabric and Chrome Tanned Leather…….61	
4.10:	Wash Fastness of the Synthesized Dyes on polyester fabric and chrome tanned leather Using ISO 3 Standard…….……..62	
4.11:	Light Fastness of the Synthesized Dyes on polyester fabric and chrome tanned leather Using 8 Blue Wool Standard……63	

LIST OF FIGURES

Figure	Title	Page
2.1	Structure of Mauveine	7
2.2	Structure of Magenta	8
2.3	Structure of C.I. Basic Orange 5	10
2.4	Structure of C.I. Pigment Blue 66	10
2.5	Structure of Sulfur Black 1	12
2.6	Structure of Congo Red	13
2.7	Structure of Copper Phthalocyanine	13
2.8	Structure of Naphthol AS	14
2.9	Structure of C.I. Acid Blue 45	15
2.10	Structure of C.I. Acid Violet 78	15
2.11	Structure of C.I. Disperse Blue 5	17
2.12	Structure of C.I. Reactive Red 6	18
2.13	Structure of Disperse Red 72	20
2.14	Structure of Blue disperse Red	20
2.15	Structure of Heterocyclic blue disperse dye	20
2.16	Structure of Indole	21
2.17	Structure of Pyrazolone	21
2.18	Structure of Pyridone	21
2.19	A thiadiazole red disperse dye	22
2.20	A nitrothiazole blue disperse dye	22
2.21	Athiophene greenish-blue disperse dye	22
4.1	Structure of the Intermediates that were diazotised	47
4.2	Structure of the Coupling Components	48
4.3	Structures of the Synthesized Dyes	48

LIST OF SCHEMES

Scheme	Title	Page
2.1:	Formation of Diazonium Salt……..…...8	
2.2:	Coupling Reaction to Form Azo Dye……..……..8	
2.3:	Mechanism of Reaction for Diazotization of Aromatic Amines……..19	
2.4:	Reaction for Formation of Polyester……31	
4.1:	Synthesis of Aminothiophene Intermediate…….45	
4.2:	Diazotization and Coupling Reaction of Intermediates 1 and 2……...46	
4.3:	Diazotization and Coupling Reaction of Intermediate 3……..…46	
4.4:	Diazotization and Coupling Reaction of Intermediate 4……..……47	

LIST OF APPENDICE

Appendix	Title	Page
I:	UV-visible Spectroscopy of Dyes……...…….....86	
II:	Infra Red Spectra of Intermediates and Dyes…….……..98	
III:	GC-MS of Intermediates and Dyes……....105	
IV:	Photographic Pictures of Dyed Substrates…….…….....108	

CHAPTER ONE

1.0 INTRODUCTION

1.1 Azo Dyes

Azo compounds are a class of chemical compounds that are continuously receiving attention in scientific research (Kirkan and Gup, 2008; Seferoglu, 2009 Otutu *et al.,* 2011). They are usually strongly coloured compounds which can be intensely yellow, red, orange, blue or even green, depending on the exact structure of the molecule. As a result of their colour, azo compounds are of tremendous importance as dyes and also as pigments for a long time (Ebenso *et al.,* 2008). For a dye to be suitable for use, the colored material must have the following desirable properties: intense colour, solubility in water and substantivity for the substrate (Nkeonye, 1987). In fact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts (Robert *et al.,* 2011; Zollinger, 2003). The structural features in organic compounds, that usually produce colour are >C=C<, –N=O, –N=N–, >C=O and $–NO_2$. Most importantly, the groups that invariably confer colour are the azo (–N=N–) and nitroso (–N=O) while the other groups actually do so under certain circumstances (Abrahart, 1977). Furthermore, azo dyes have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium (Samieh *et al.,* 2008), toner (Kirkan and Gup, 2008), ink-jet printing and oil-soluble light fast dyes (Gregory, 1990). Recently, azo compounds as organic dyes have also attracted attention due to their interesting electronic features in photoconductors (Yildiz and Boztepe, 2002). However, the traditional application field of the synthetic azo dyes still remains the textile industry, and the finishing of fibrous materials.

In recent years, several heterocyclic and non heterocyclic compounds are extensively used in azo dye chemistry for textile and non-textile applications (Katritzky and Rees, 1984). These dyes are now marketed to produce a full range of azo dyestuffs without the use of colorants based on hetero-aromatic diazo components. Most of the heterocyclic dyes are

derived from the diazo components consisting of five-membered rings containing one or more nitrogen heteroatoms, with the rings being fused into another aromatic ring (Griffiths *et al.*, 1984; Towns, 1999; Samieh *et al.*, 2008; Otutu *et al.*, 2011). The dyes with heterocyclic diazo components have been intensively investigated, to produce bright and strong colour shades ranging from red to greenish blue on synthetic and natural fibres. These results led to commercial products to replace the conventional azobenzene dyestuffs. The nitro substituted aminothiophenes, and aminothiazoles are primarily of importance as diazo components (Seferoglu, 2009). Non-textile uses of heterylazo disperse dyes have been explored, for example in reprographic technology, functional dye applications, and non-linear optical systems (Zollinger, 2003). The monoazo dyes containing heterocyclic rings or carbocyclic rings result in brighter and often deeper shades than their disazo or trisazo analogues. On the other hand, the disazo or trisazo dyes are very important in applications such as disperse dyes for polyester fibres, and as photoconductors (Otutu *et al.*, 2011).

The past few decades have witnessed considerable innovation in the field of azo dye chemistry based on heterocyclic systems and studies in the synthesis of such derivatives have been reported (Alaa and Terek, 2006; Maradiya, 2010). Heterocyclic based azo dyes are not only important for their excellent properties as dyes for polyester textiles; they have also been utilized in non-textile applications such as photodynamic therapy, lasers, reprographic technology, functional dye applications and non-linear optical systems. Although a variety of heterocyclic and conventional azo benzene systems have been employed for the synthesis, there remains much scope for the design and development of new chromophores. Most of the recent research has focussed on structural variations of existing types, for example variations in substituents, especially on the side chains of the coupling components (Alaa and Terek, 2006; Maradiya, 2010)

.

1.1.1 Disperse Dyes

Disperse dyes are sparingly water soluble dyes. The most important class of disperse dyes 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 also 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. 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).

1.1.2 Acid Dyes

Acid dyes are water soluble dyes which are applied basically from acid solution onto fibres possessing basic nitrogen groups e.g. leather, wool, silk, nylon. The water solubility is as a result of the presence of sulphonic acid groups or in rare cases carboxylic acid groups. Acid dyes are found in nitrophenols, azo compounds, triphenyl methane, anthraquinoids or indigoid compounds (Recep, 2005). There are three kinds of acid dyes which are in accordance to their molecular mass and ease of levelling. Those of higher molecular mass which do not level easily (groups 2 and 3) are known as acid milling and neutral milling dyes (Nunn, 1979).

1.2 Statement of the Research Problem

Most of the conventional azobenzene dyes fall in the visible region of the spectrum and hence not sufficiently bathochromic and this place a limitation on the colours obtained. Therefore there is need to synthesize dyes that are highly bathochromic and possess good colouristic properties.

The growth of micro-organisms on textile materials inflicts a range of negative effects not only on the fibre itself but also on the wearer. This is due to the fact that fibrous materials undergo biological degradation, and it seems that about 40 % of the damage is due to the effect of microorganisms.

In spite of decades of effort it has been difficult to obtain fibrous materials free of pathogenic microbes. To survive bacterial developed antibiotics mechanism, there is a great demand for new dyes with good colouristic and application properties, and also exhibiting biological activity.

1.3 Justification

Azo compounds are versatile molecules and have received much attention in both research, and application (Nejati *et al.*, 2007).

Due to the smaller molecular size of the mono-azo dyes, they are expected to present good penetrability in fibre, and the exhaustion problem of acid and disperse dyes on fibres improved. This will reduce the amount of dyes left after dyeing, thus reducing the environmental pollution caused by the use of acid and disperse dyes (Hallas and Towns, 1997a).

The present study is focused on the possibility of developing new azo dyes with good colouristic and application properties, and exhibiting biological activity.

1.4 Aim and Objectives of the study

Aim

The aim of this research was to synthesize acid and disperse dyes using aminothiophene and conventional amine based diazo components and to study their application and antimicrobial properties.

Objectives

The main objectives of the present study were:

1. To synthesize series of azo acid and disperse dyes based on 2-aminothiophene and conventional amines as diazo components, and with coupling components such as N,N-dimethylaniline, N,N-diethylaniline and dodecyl-pyridone.
2. To characterize the structure of the dyes using Uv-visible, FT-IR Spectrophotometry and GC-MS.
3. To investigate the dyeing properties of the synthesized heterocyclic disperse dyes on polyester fabric and acid dyes on chrome tanned leather.
4. To investigate the fastness properties of the dyed substrates to agencies such as washing and light.
5. To investigate the antimicrobial properties of the synthesized dyes against some selected bacteria and fungi such as *Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, Candida krusei, Candida albicans and Aspergillus niger.*

CHAPTER TWO

2.0 LITERATURE REVIEW

The art and science of dyes began more than 10,000 years ago. The very first dyes may have been crude compounds made from plants mixed with water by early uncivilized man for the purpose of tribal rituals, to identify or differentiate class of status group or simply amuse children with colours (Shore, 1990).

A dye is an organic substance used to impart colour to other materials by dyeing or pigmentation. Dyes are used to colour natural fibres such as cotton, silk, wool and linen and synthetic fibres, such as nylon, cellulose acetate and polyester. They are also used on other type of substrates such as leather, wood, food, paper and in photography. Dyes for home use are the same as those used in industry and they are applied by same methods (Iyun, 2008).

2.1 Development 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. But synthesis and manufacture of a purple dye by Perkin W.H in 1856 is rightly regarded as the beginning of the synthetic dye era (Allen, 1971). In that year, William H. Perkin the son of a builder was sent to the City of London School, where he showed aptitude for chemistry, and was under the guidance of Hoffman, the celebrated German chemist.

Perkin at the age of eighteen was attempting to synthesize the antimalaria drug quinine by oxidizing aniline with acidified potassium dichromate. He obtained a black precipitate which he extracted with naphthol and then with ethyl alcohol to obtain a brilliant purple solution. Further work on this experiment led him to conclude that they had produced a useful dyestuff. Perkin’s work was of a profound significance because this was the first

time a chemist had produced 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. Perkin sent a sample of his dye to Pillar of Perth, who tried it out in their dyeing works and gave it a favourable report. Perkin therefore, at eighteen, assisted by his father and brother, built a factory at Greenford near London. He then devised and erected a 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 Perkin 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.

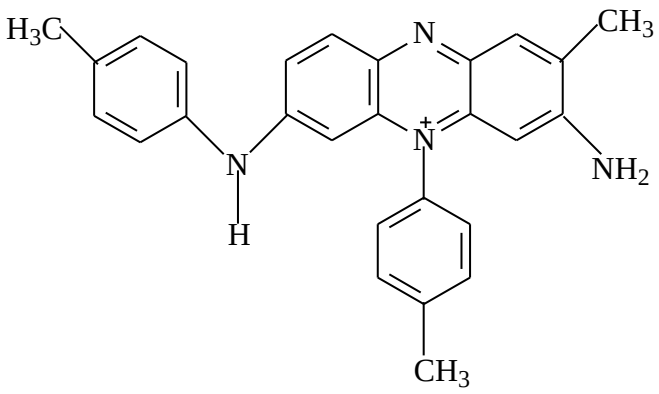


Fig. 2.1: Mauveine

The birth of the synthetic organic dyestuff industry in 1856 was followed by a total dependence on coal tar as a source of aromatics for virtually the next 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).

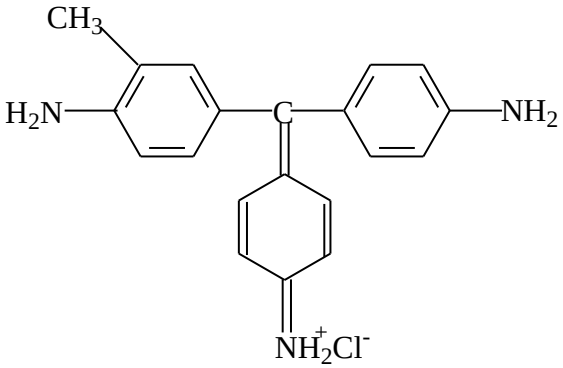
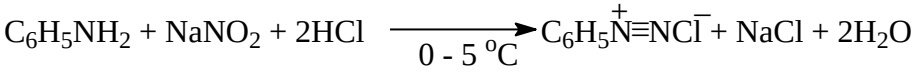


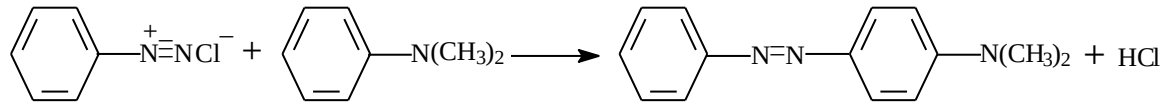
Fig. 2.2: Magenta

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:



Scheme 2.1: Formation of Diazonium Salt

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 aminoazobenzene

Scheme 2.2: Coupling Reaction to form Azo dye

Some of the earliest dyes based on this reaction were Bismark Brown by Martius in 1865 and Chrysoidine G 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 hydroxylazo-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 had 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.

2.1.1 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 and 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 Perkin in England produced many dyes originally called Hoffman violets, some of which still survive till today which were Methyl Violet and Crystal Violet; the latter 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, Induline, Eosine, Chrysoidine and Methylene Blue dyes and so forth (Beer, 1959), and 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 tinctorial properties; their importance nowadays lies in their suitability for the dyeing of acrylic fibres. An example is the C.I Basic Orange 5 as shown in Figure 2.3 below:

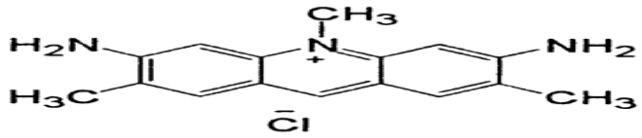


Fig 2.3: C.I Basic Orange 5

2.1.2 Vat dyes (Indigoid)

Baeyer, a German chemist synthesized indigotin in 1880 and created a great scientific interest among the chemists 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 indigo 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). An example is C.I. Pigment Blue 66 as shown in Figure 2.4 below.

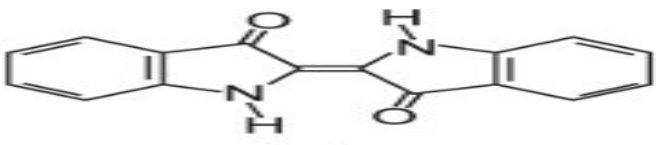


Figure 2.4: C.I. Pigment Blue 66

2.1.2.1 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 systems 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 synthesise 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).

2.1.2.2 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).

2.1.3 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 sodium sulphide (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 inspite of their long history, consequently they are classified according to the chemical structure of the organic intermediates from which they are derived (Allen, 1971). An example of sulphur dye is Sulfur Black 1 in Figure 2.5 below

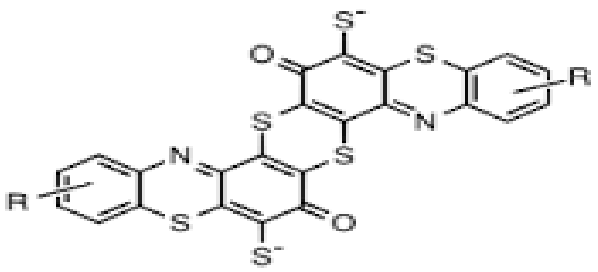


Figure 2.5: Sulfur Black 1

2.1.4 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. Atypical example is Congo Red as shown in the Figure 2.6 below.

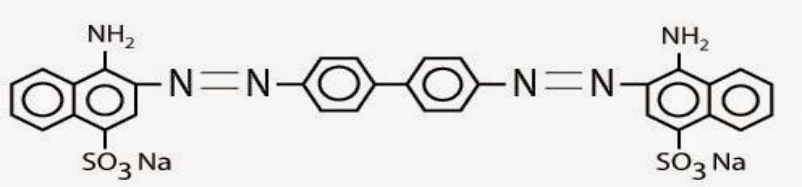


Figure 2.6: Congo Red

2.1.5 Phthalocyanine dye

An event of great interest in the chemistry and technology of dyes was the manufacture of copper phthalocyanine, Monastral Fast Blue BS (ICI) in 1934. 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.

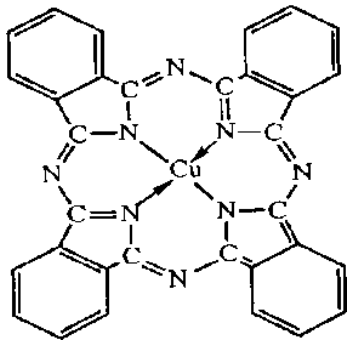


Fig. 2.7: Copper Phthalocyanine

2.1.6 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. The anilide of 2-hydroxy-3 naphthoic acid had a significant affinity for cellulose and was made by Schopff in 1892, but its advantage as a coupling component was 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).

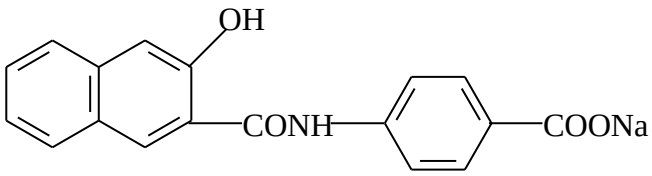


Fig. 2.8: Naphtol AS

2.1.7 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 the 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). A typical example of an acid dye is C.I. Acid Red 73 as shown in the Figure 2.9 below.

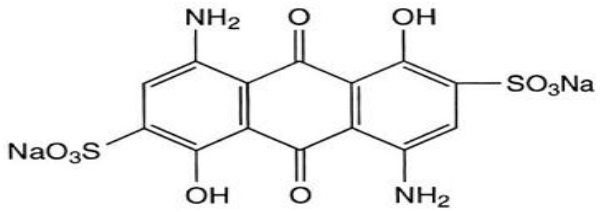


Figure 2.9: C.I. Acid Blue 45

2.1.8 Metal Complex dyes

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. An example of a metal complex dye is the C.I. Acid Violet 78 as shown in Figure 2.10 below.

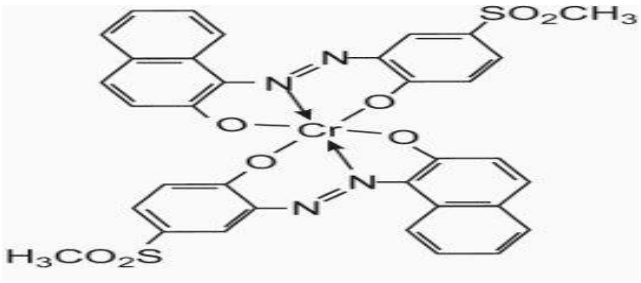


Figure 2.10: C.I Acid Violet 78

2.1.9 Disperse dyes

The development of disperse dyes is inextricably linked with the development of synthetic fibres in 1938 when Du Pont de Nemours and co introduced the first synthetic fibre known as nylon. In 1959 E.I. Du Pont 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. Before then, the quantity of disperse dyes used for colouring the above named synthetic fibres were very small and only limited to pale shades 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 Du Pont proved to be major land marks in the history of disperse dyes since they were the only class 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 which allowed the use of temperatures typically 130^0C above atmospheric pressure which speeded up the 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 who 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, 1987). Vickerstaff and Walters in 1954 obtained the isotherm and concluded that the mechanism was that of colloidal solution of the dye in fibre. Bird (1975) 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 thermodynamics of dye sorption also pointed out the similarities between solid solution and Langmuir adsorption. Today, there is a general acceptance of Clavels 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 dyes 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). An example of disperse dye is C.I. Disperse Blue 5 shown in Figure 2.11 below.

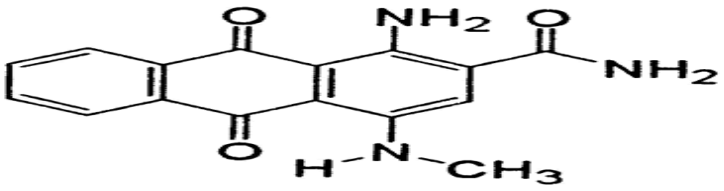


Figure 2.11: C.I. Disperse Blue 5

2.1.10 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 when he then realized that a dyeing of high washing fastness with no staining of adjacent undyed material had been 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. A typical example is C.I. Reactive Red 6 as shown in Figure 2.12 below.

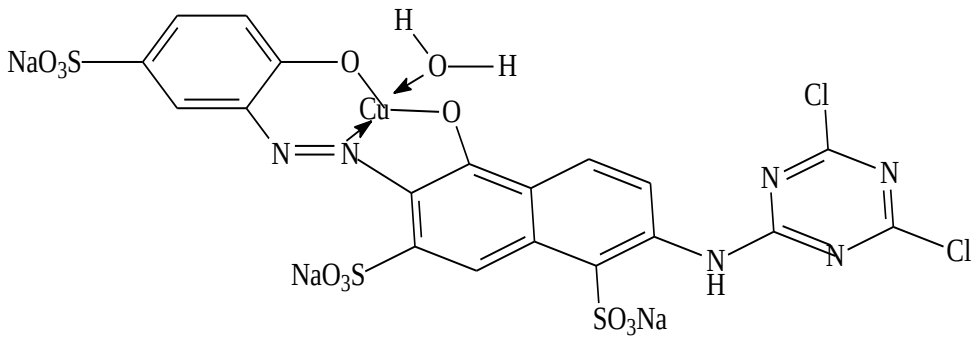
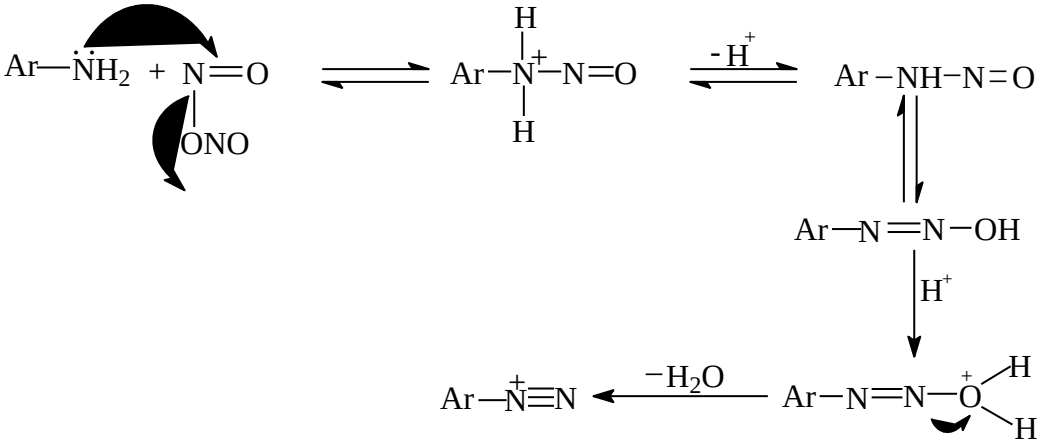


Figure 2.12: C.I. Reactive Red 6

2.2 Azo dye synthesis

Azo dyes are synthesized by a two stage process (diazotization and coupling) which has remained almost unchanged since its discovery by Greiss in 1861.

Diazotization typically involves the treatment of a primary aromatic amine ($ArNH_2$) with nitrous acid. The first stage involves a nitrosation reaction and the exact nature of the nitrosating species varies with the reaction conditions used.Thus in the aqueous process ,a solution of the sodium nitrite is added to a solution or suspension of the amine in hydrochloric acid ,and it has been suggested that the nitrosating species is dinitrogen trioxide (N_2O_3) as shown below (Abrahart,1977)



Scheme 2.3: Mechanism of reaction for diazotization of aromatic amines

Weakly basic amines (e.g. 2,4-dinitroaniline) require sulfuric acid for diazotization, and this involves the formation of nitrosyl sulfuric acid ($NO^+HSO_4^-$) obtained by adding concentrated sulfuric acid to solid sodium nitrite , when the nitrosating species may be NO^+ or $HOSO_2ONO$. Aminophenols and aminonaphthols on the other hand require mild diazotizing conditions due to the risk of the formation of quinones under the oxidizing conditions of this process.

Commercially important diazo components include chloroanilines, nitroanilines, 2-aminophenols and aminonaphthols, the last two being used to build metalizable groups into azo dyes for cotton and wool, and heterocycles such as 2-aminothiophene and 2-aminothiazoles which are used in azo disperse dyes for polyester.

The diazonium cation used in azo dye synthesis is a weak electrophile and will undergo an electrophilic substitution reaction with suitably activated coupling components. These components are typically:

(a) Substituted amines- as in the production of disperse dyes for polyester and basic dyes for acrylics

(b) Substituted naphthols- as in the synthesis of acid and mordant dyes for wool and direct and reactive dyes for cotton

(c) Enolisable ketones– used especially for yellow–orange pigment.

The coupling reaction between diazonium ions and amines take place under slightly acidic conditions. This sequence is particularly important in the manufacture of amino azobenzene disperse dyes for polyester. Typically the diazo component contains electron-withdrawing groups (NO_2, CN) and the amine coupling component contains electron donors (NR_2, OCH_3, $NHCOCH_3$). Increasing degrees of substitution extends the colour range from orange through red to blue as shown in Figs. 2.13-2.14 (David and Roy, 1989).

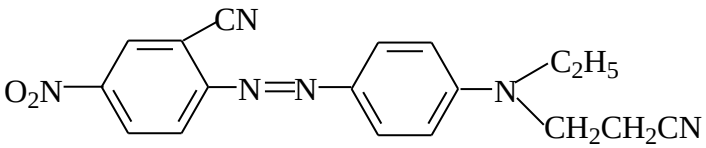


Fig 2.13: Disperse Red 72

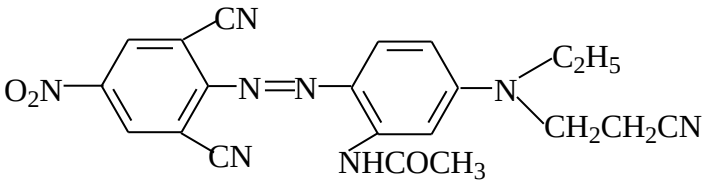


Fig 2.14: Blue Disperse dye

The use of heterocyclic diazo components is now becoming a prime area of research by dye chemists and remarkable successes have been recorded. The colour range of these dyes extends to blue and blue green, hitherto the exclusive domain of the anthraquinones. Figure 2.15 shows the structure of a blue disperse dye prepared using 2-amino-3, 5-dinitrothiophene as the diazo component.

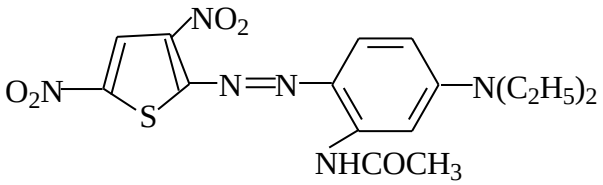


Fig 2.15: Heterocyclic blue disperse dye

Although hydroxyl groups are known to be electron donors, they are less efficient in arylazo phenol versus aryazo naphthol structure. This is because the naphthol system does not

lose full aromatization when electron delocalization occurs. Therefore, Naphthol couplers generally give dyes that are more bathochromic than phenol-based dyes.

2.3 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 pyridines shown below in Figs. 2.16-2.18.

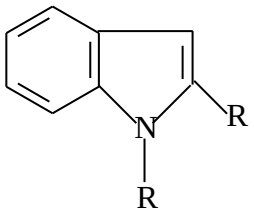


Fig. 2.16: Indole

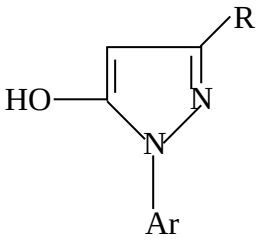


Fig. 2.17: Pyrazolone

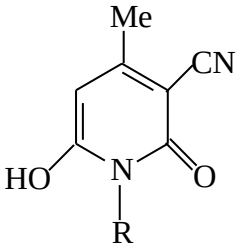


Fig. 2.18: Pyridone

Heterocyclic compounds have been utilized as coupling components in preparing azo dyes for polyester, in addition to diazonium components, but, according to the volume of patent literature, less emphasis seems to have been expended towards their use as couplers. However, one series of heterocyclic couplers which has achieved spectacular success consists of the so called pyridine couplers. Azo dyes from these couplers on polyester produce bright yellow dyeing with particularly high light fastness, excellent dyeing and other fastness properties. One important feature of these dyes is their particularly high extinction coefficients, which together with the ready availability of raw materials for the coupler and the dye's ease of synthesis, make for an economic combination of properties.

In contrast to the heterocyclic coupling component, all the heterocyclic diazo components that provide important azo dyes contain sulfur, either alone or in combination with nitrogen .These S or S/N heterocyclic azo dyes provide bright, strong shades that range from red to blue and therefore, complement the yellow/orange colours of the nitrogen heterocyclic azo dyes in providing a complete coverage of the entire shade. Representative dyes are the thiadiazole red , the nitrothiazole reddish blue and the thiophene greenish-blue as shown in figures 2.19-2.21 (El-Kashouti *et al.*, 2008).

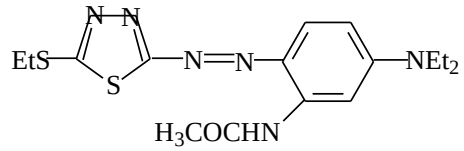


Fig 2.19:A thiadiazole red disperse dye

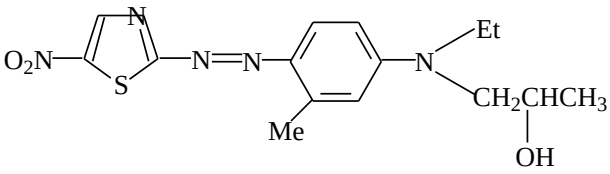


Fig 2.20: A nitrothiazole blue disperse dye

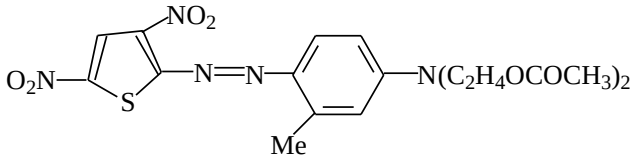


Fig 2.21: A thiophene greenish-blue disperse dye

2.4 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 bonds. 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).

2.5 Dyes and their Required Properties

A dye is a deeply coloured organic compound usually soluble in water, but not all coloured compounds are textile dyes. Some are only useful as indicators in chemical titration (e.g. methyl orange), while some are used as stains or solvent dyes for colouring solvent such as petrol, etc. (Nkeonye, 1987).

For a dye to be useful as a textile dye, it must have the following properties:

(a) Intense colour-arising mainly from charge transfer.

(b) Attraction or affinity for the fibre.

(c) Substantivity; capable of being absorbed and retained by the fibre after application and/or fixation, and reactivity, -ability to be chemically combined with the fibre.

(d) Sufficient degree of resistance (fastness) to common agencies encountered during use of the coloured material e.g. light, water, rubbing, etc.

(e) Solubility in aqueous solution either permanently or during the dyeing operation. This is because the dyes are usually in form of salts.

In addition to colouring textiles, some textile dyes can be used to colour substances such as paper, leather, fur, etc.

2.6 Forces of Attraction between Dye and Fibres during Dyeing

In order to obtain a clear view of the mode of attraction of the dye to the fibre, knowledge of the forces which bind the dyes to the fibres is of obvious importance in the present review. In most dyeing processes, the material to be dyed is brought into contact with a transfer medium containing the dye. The most common transfer medium is water, in which the dye may be dissolved or dispersed. During dyeing the dye passes from this solution or dispersion into the fibre. The transport of the dye from the solution into the fibre may be regarded as entailing three steps viz: transfer of dye from the bulk of the solution to the fibre

surface, adsorption of dye at the fibre surface, and penetration of the dye from the surface into the interior of the fibre substance (Nkeonye, 1987).

The first action in any dyeing operation is therefore the concentration of the dye molecules at the internal surface of the fibre. The concentration so produced is however, not usually sufficient to give a usefully deep colouration and fastness properties required of a dyed material. It is required that the dye be associated strongly with the fibre to make it resistant to such agents as water, detergents, perspiration, weather, solvent etc (Ugbolue and Alula., 1980).

For this to be achieved, other factors must be brought into play. These are the chemical forces which can operate between a dye molecule and a fibre molecule, and also those between the dye molecules themselves which can cause their association into larger units. These forces have been classified as ionic forces, hydrogen bonding, covalent bonding and Van der Waals forces (Derbyshire and Peter, 1955; Rattee, 1974).

2.6.1 Ionic Bonds (Ionic Forces)

This is the mutual attractions between positives centres in a fibre and negative centres in a dye molecule and between negative fibre sites and positive centre in a dye molecule. This is the case when an atom transfers its electron to another atom, the one that lost the electron in the effect becoming positively charged while the atom that received the electron will become negatively charged. These types of forces play a large part in the dyeing of protein fibres with acid and direct dyes, nylon with acid dyes and polyacrylics with basic dyes (Abrahart., 1977).

2.6.2 Hydrogen Bonding

This results from the acceptance by a covalently bound hydrogen atom of a lone pair of electrons from an electron donor atom. Hydrogen bonding can act in five different ways:

i. intermolecularly extending over many molecules,

ii. intermolecularly joining two molecules together,

iii. intermolecularly where the electron donation is by double bond linkage,

iv. intramolecularly forming a chelate ring and

v. intramolecularly as ion in hydrogen fluoride (HF_2)

Hydrogen bonding has some properties of normal valency bonding. They interact when the atoms approach within very close distance to each other. They are relatively of the order of 8.4-49.4 $kJMol^{-1}$. They are relatively easy to form and break. Hydrogen bonding occurs in most dye-fibre systems.

2.6.3 Covalent Bonding

These are chemical bonds between dyes and substrate molecules. They are brought about by chemical reaction between a reactive dye molecule and the substrate molecule, example hydroxyl group of a cotton fibre. In fact covalent bonding has to do with primary valency bonding where each of the participating atoms has to donate one electron to the common linkage. This is the strongest of all dye–fibre bonds. They have the highest energy of about 84kJ/Mol. Covalent bonding is the bond responsible in reactive dye bond in leather, wool and nylon.

2.6.4 Van der Waals Forces

These are forces existing between atoms and molecules of all substances and are small compared with the other inter- atomic forces present in the dyeing process. They are the result of second order wave mechanical interaction of the pi-orbital of dye and fibre molecules. These forces are especially effective when the dye molecules are linear, i.e. long and flat and can approach close enough to the fibre molecules or molecular unit.

2.7 Hides and skins

Hides and skins are derived from human beings, a mammal,- the size of an elephant or a mouse, a bird like, - an ostrich or a sparrow, a small sardine or a huge shark, a lizard or a crocodile, with structure having certain features in common.

Hides or skins vary in thickness and have distinct patterns peculiar to the species. Hides normally are thicker than skin. Every hide or skin consists of three distinct layers:

i. the upper layer called epidermis or cutis,
ii. the middle layer called corium or dermis and
iii. the flesh layer called hypodermis (Sarkar, 1980).

2.7.1 Functions of Hides and Skins

i. It provides a light, durable covering for the body.
ii. It helps to regulate the body temperature.
iii. It prevents or minimizes injury to vital organs and acts as a barrier to bacteria infection.
iv. It presents a waterproof surface to the outside, while allowing moisture (sweat) to reach its surface from inside.
v. It is flexible, stretching and contracting with its wearer's movement.

During processing of hides and skins, it is desirable to retain all the above mentioned characteristics and to alter them as little as possible. Booths and shoes made from plastics or other synthetic compounds are more uncomfortable in wear as these substances do not permit the free passage of perspiration.

2.7.2 Tanning

This is the process for converting hides or skins into leather, a form which makes them resistant to decay, while increasing their wearing qualities inherent in the living hides or

skin. The art of tanning started when man first killed animals for food and removed their hides as a covering for him and family. Experience taught him that untreated dry hides were hard, so he rubbed them with stones using the brains and marrow of the slain beasts. They also used smoke to preserve hides. Alum, gallnuts, tree barks, pods and leaves have all been used from very early times for producing leathers. The footwear and other leather goods found in a well preserved state in ancient Egyptian tombs give an adequate illustration of the skill and craftsmanship achieved during the early period. The art of tanning advanced considerably during the middle ages. In those times, science and art of tanning were kept secret, such knowledge, usually were being passed from father to son. Today, tanning processes are not such close secrets. No matter what hide or skin is to be processed, the procedure is the same; the removal of the undesirable parts (epidermis and hypodermis) and the rendering of the dermis strong, flexible and resistant to putrefaction (Mann, 1969).

2.7.3 Tanning Procedure

The hide or skin is soaked in vats to wash away adhering blood, dirt or dung, return the moisture removed during their drying or salting or to make certain parts easily removable and facilitate the penetration of chemicals. Soaking of hides takes up to 72 hours depending on the thickness. After soaking, liming proceeds. This process takes up to 14 days. Liming is done to separate the epidermis so that it and the hair may easily be removed from the dermis. It also breaks down and removes some of the fats and causes swelling and plumping of the fibres. During liming, hides that are heavily damaged by putrefaction as to render them unsuitable for leather are sorted out. The softened epidermis and the hair are removed by either machine with revolving rollers or by hand. After this stage, it is washed thoroughly with running water in a revolving drum. The hide is then digested by a process called bathing in order to remove certain undesirable proteins. This takes about 30 minutes and leaves the hides or skin soft and silky. In the past, droppings of domestic fowls or dogs were used as

reagent for bating; presently pancreatic enzymes and ammonium chloride are used. The above enumerated process is only to prepare the true dermis for tanning (Mann, 1969). Tanning can either be vegetable or mineral.

2.7.3.1 Vegetable tanning

Tannins are bitter astringent principles found in root, bark, leaves or galls of various trees. They have the property of combining with the fibres of the hides or skins rendering them more resistant to decay. In the Northern Nigeria, the main source of vegetable tannin is from the pods of *Acacia arabica* (Bagaruwa H) and wattle bark is also commonly used (Mann, 1969). Vegetable tanning are divided chemically into two groups namely pyrogallol and catechol (pyrocatechol). These classifications were made based on the substances obtained on dry distillation of vegetable tanning materials (Sarkar, 1980).

Tannin extracts are prepared by leaching the finely chopped plant material with water. The liquor is then concentrated in vacuo to yield a vicious semi solid mass, which hardens on cooling. Vegetable tanning is a slow process if compared to chrome (mineral) tanned leather requiring from 25 to 100 days depending on the thickness of the hides or skin. Tanning is carried out in vat containing tannins in various concentrations and with different degrees of acidity depending on the substrate and the required shade. The hide or skin is immersed in the weakest solution and is moved to a more concentrated one every few days. In the stronger solution, the tannin penetrates deeper into the hide and is deposited between the fibre bundles (Muralidharan and Rao, 2005).

2.7.3.2 Mineral tannin (chrome tanning)

This is a very rapid tanning process, taking only few hours for complete tanning. The process is simple. Chrome tanned leather is popular with the consumers because of its light weight, durability and its resistance to heat. It is also easily dyed and finished.

The chrome used for the tanning belongs to a group of elements known as trivalent, usually representing one valency linkage. A typical salt of trivalent chrome is Cr_2O_3. The hide or skin fibre has the power of absorbing and permanently fixing only the basic salt whereby the fibre is tanned or converted into leather (Sarkar, 1980). The effluent generated via chrome tanning is difficult to manage. Leathers produced by chrome tanning can be very hard when compared with the vegetable tanned leather, but may be deficient in water proof qualities unless filled with grease or wax, a process referred to as resin finishing. In other words, the water resistance property of vegetable tanned leather is preferred to that of chrome tanned leather. Water resistance is a very good property for leathers for shoe upper and military and paramilitary boot.

2.7.4 Dyestuffs Available for the leather Industries

Dyes for these substrates normally form ionic bonds within the polymer matrix. In this case dyes bearing a negative (anionic) charge are used because proteins such as wool, silk, and leather carry a positive (cationic) charge – especially during the dyeing process. Anionic dyes for protein substrates are known as acid dyes, an example of which is C.I. Acid Black 1.They derive their name from the fact that they are typically applied to suitable substrates from a medium containing acid. These dyes have little to no affinity for polyester, cellulosic, or cationic polymers, since such substrates cannot form an ionic bond with them.

Leather dyes do not have their own colour index generic name as obtained in other substrates but are either acid, direct, mordant or reactive types and appear in the colour index where a leather usage has been suggested by a manufacturer (Tysoe, 1994).

2.7.5 Dyeing of Leather

Leather is dyed to improve its appearance and make it saleable in a finished form. Leathers have inherent pigmentation and grain characteristics, which together with other

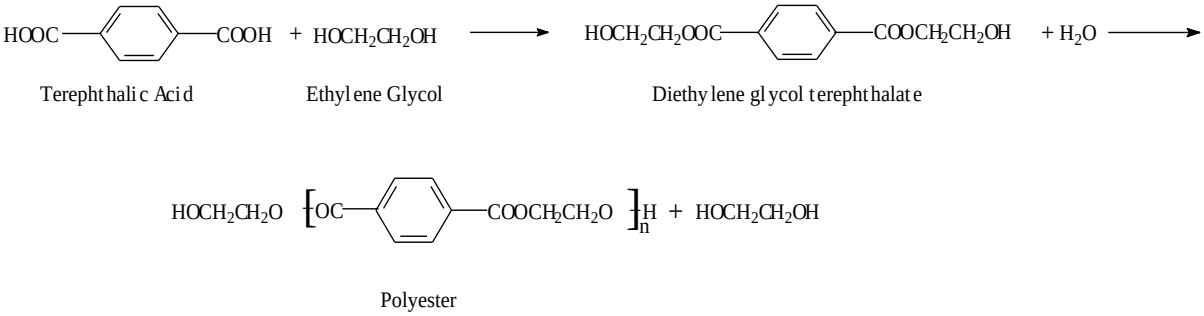
factors make attainment of uniformity of shade throughout the piece difficult if not impossible to attain; but this makes leather difficult to duplicate synthetically and this factor gives it psychological appeal. A variety of dyeing procedures are in commercial use, including drum, spray, paddle, brush, tray and solvent dyeing. The first two are the most applied techniques. Dyeing temperature is controlled within the range 25-60 ^{o}C and the pH is set in the range 3.8–5.5. Liquor ratio is generally low, example in drum dyeing, 2-8 times the weight of leather (Traubel and Eitel, 1977).

2.7.6 Dye selection for leather application

Leather dyes are selected based on the hue of the dye, application, properties (solubility, levelness, and penetration), fastness properties and the tinctorial strength or cost factor. Brown and black shades remain the most important leather colours representing about 85 % of the total market. Because dyeing is done at low temperature, dyes must be soluble in the 40-65^{o}C range. Solubility in weak acids is also important as dyes are applied at weakly acidic pH (3.8 -5.5) (Venkataraman, 1978).

2.8 Polyester Fibre

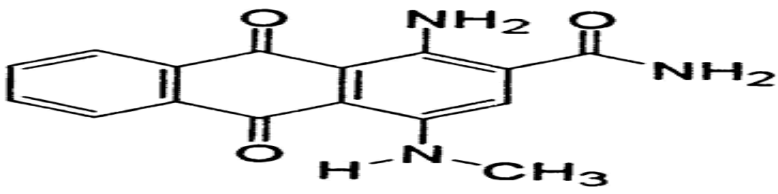
Polyesters are those fibres containing at least 85% of a polymeric ester of a substituted carboxylic acid including but not restricted to terephthalic acid and hydroxybenzioc acid. The major polyester in commerce is polyethylene terephthalate (Chatterjee, 1988; Gohl and Vilensky, 1980), an ester formed by step growth polymerization of terephthalic acid and ethylene glycol at 250-300^{o}C in the presence of a catalyst to a DP of 100-250.



Scheme 2.4: Reaction for Formation of Polyester

2.9 Dyes for polyesters

Dyes developed for polyesters are known as disperse dyes. In this case, the mechanism of coloration involves "dissolving" the dye in the polymer matrix to form a solid–solid solution. Taking advantage of the well known principle that "like dissolves like", disperse dyes are designed that are hydrophobic in nature. Such colourants are very sparingly soluble in water and derive their name from the fact that they are dispersed rather than fully dissolved in water to carry out the dyeing process. An example is C.I. Disperse Blue 165. Disperse dyes have no affinity for hydrophilic polymers such as cellulose, which makes them unsuitable for colouring cotton, cellophane, and paper, but quite suitable for poly(ethylene terephthalate) and cellulose acetate. An example of disperse dye for polyester fabric is C.I. Disperse Blue 5 as below.



See Figure 2.11: C.I. Disperse Blue 5

2.10 Antimicrobial Dyes

Man has adopted antimicrobial substances since ancient times, a fact that is demonstrated by their use in Egyptian mummies and in similar applications in other cultures. In this regard, the protection and preservation of fabrics, too, have long fulfilled a role of the

utmost importance. The need to protect and preserve is still fundamental in many textile applications today. Antimicrobials are protective agents that, being bacteriostatic, bactericidal, fungistatic and fungicidal, also offer special protection against the various forms of textile rotting (Thoraya *et al.,* 2008).

Azo dyes are among the compounds which are suitable for biocidal treatment of textile materials due to the fact that some of them exhibit biological activity, as a result of the presence of some bioactive templates that form a definite type of bonding with the molecules of the fibrous materials (Simu *et al.,* 2010).

The existence of an azo moiety in different types of compounds has caused them to show antibacterial and pesticidal activities. In the recent times, exploration of azo dyes as antimicrobial agents has received considerable attention (Gopalakrishnan *et al.,* 2011; Shridhar *et al.,* 2011; Patel, 2012; Avci *et al.,* 2012).

Antimicrobial finishes that control the growth and spread of microbes are more properly called biostats, i.e. bacteriostats, fungistats. Products that actually kill microbes are biocides, i.e. bacteriocides, fungicides. This distinction is important when dealing with governmental regulations, since biocides are strongly controlled.

Despite the long list of requirements, a variety of chemical finishes have been used to produce textiles with demonstrable antimicrobial properties and one of which is the use of azo dyes. The dyes used for antimicrobial finish consists of molecules that are chemically bound to fibre and these dyes can control both microbes that are present on the fibre surface or in the interior of the fibre (Khalid *et al.,* 2008)

Two different aspects of antimicrobial protection provided by chemical finishes can be distinguished. The first is the protection of the textile user against pathogenic or odour causing microorganisms (hygiene finishes). The second aspect is the protection of the textile itself from damage caused by mould, mildew or rot producing microorganisms. Bacteria are not as damaging to fibres, but can produce some fibre damage, unpleasant odours and a slick,

slimy feel. Often, fungi and bacteria are both present on the fabric in a symbiotic relationship (Bellini, 2001; Heywood, 2003)

A typical example is the use of antimicrobial cationic dyes in dyeing acrylic fabrics. It was found that these functional dyes could be effectively introduced to acrylic fibres to achieve simultaneous coloration and functional finishing effects. All the dyed fabrics exhibited antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*. The washing durability of antimicrobial functions on the treated fabrics was further studied (Ma and Sun, 2005).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

Analytical grade reagents and chemicals from Sigma Aldrich Chemical Company were used for this research work. These include; N, N-diethylaniline, sulphanilic acid, N, N-dimethylaniline, dodecylpyridone, hydrochloric acid, sodium hydroxide, conc. sulphuric acid, ethanol, methanol, acetone, o-Acetoacetanilide, malononitrile, sulphur, morpholine, acetic acid, propionic acid, sodium nitrite, dimethylformamide (DMF), dimethylsulphoxide (DMSO), gamma acid, N-(2, 4-dimethylphenyl)-3-oxobutyramide and urea. They were all used without further purification. Other materials were chrome tanned leather and polyester fabric.

3.2 Apparatus and Equipment

Thermometer, pH meter, heating mantle, magnetic stirrer, electronic balance, Gallenkamp melting point apparatus, Agilent CARY 300 UV-visible spectrophotometer, Agilent CARY 630 FT-IR, Electric Oven, beakers, round bottom flask, 250ml volumetric flasks, Buchner flask, hot plate, steam bath, sample bottles, Agilent Gas chromatography-mass spectrometry (7890B GC System).

.

3.3 Synthesis of Aminothiophene Intermediates

The aminothiophene intermediates 1 and 2 were synthesized following the Gewald's methods reported by Alaa and Tarek (2006) as outlined below.

3.3.1 Aminothiophene intermediate 1

Ortho-acetoacetanilide (21.16 g, 0.1 mol), malononitrile (6.96 g, 0.1 mol) and sulphur (3.37 g, 0.1 mol) in 30 ml ethanol were stirred in the presence of morpholine (8.97 g, 0.1

mol) at 70 ^{o}C for 3 hours. The resulting thick dark solution was cooled and stored overnight in a refrigerator, followed by filtration, washing with ethanol and then ethanol/water (1:1) solution and dried. The light brown powder obtained was then recrystallized from ethanol.

3.3.2 Aminothiophene intermediate 2

Morpholine (8.92 g, 0.1 mol) was added to a mixture of N-(2, 4-dimethylphenyl)-3-oxobutyramide (20.72 g, 0.1 mol), malononitrile (6.96 g, 0.1 mol), sulphur (3.37 g, 0.1 mol) and ethanol (30 ml) at 50 ^{o}C. The mixture was stirred at 70 ^{o}C for 3 hours. The resulting solution was cooled down by adding crushed ice and placing it in a refrigerator overnight, followed by filtration, washing and drying. A brown powder was obtained which was recrystallized from ethanol.

3.4 Purification and Determination of some Physical properties of the Synthesized 2-Aminothiophene Intermediates

The 2-aminothiophene intermediates 1 and 2 were purified by three to four recrystallizations from ethanol. A known weight of the intermediate was dissolved in small quantity of ethanol and heated up with constant stirring. It was then filtered off while cooling using a Buchner funnel with a suction pump. The crystals were collected, washed several times with water and dried. After the recrystallization, the purity of each heterocyclic amine was checked by spotting on a TLC plate using Hexane : ethyl acetate (2:1) as the eluent (Maradiya, 2001) and the melting point was also determined.

3.5 Procedure for Diazotization and Coupling

3.5.1 Diazotization of Intermediates 1 And 2

Sodium nitrite (1.38 g, 0.02 mol) was added drop wise to 10 ml of concentrated sulphuric acid at 10 ^{o}C with stirring for 15 min. The solution was cooled to 5 ^{o}C on ice bath. A mixture of acetic acid and propionic acid (17:3) were added to the mixture with constant

stirring. The finely ground aminothiophene intermediate 1 (5.14 g, 0.02 mol) was slowly added within 30 minutes below 5 ^{o}C and the whole mixtures was stirred at 0-5 ^{o}C for 3 hours. The excess nitrous acid (tested for, using starch iodide paper) was decomposed with the required amount of urea.

The same procedure was repeated for aminothiophene intermediate 2 (5.70 g, 0.02 mol), and thereafter, the clear diazonium salt solution thus obtained was used immediately in the coupling reaction.

3.5.2 Diazotization of Intermediate 3

Sulphanilic acid (3.5 g of 0.02 mol) was dissolved in 30 ml of 2 M solution of NaOH. The solution was then cooled in an ice bath. A solution of sodium nitrite (50 ml of 1 M) and 10 ml cold solution of Conc. HCl was added drop-wise with continuous stirring for 30 min to form the diazonium salt solution.

3.5.3 Diazotization of Intermediate 4

The diazotization was carried out by first adding copper sulphate solution to the solution of Gamma acid (1.20 g of 0.011 mol) in water at 20 ^{o}C, followed by addition, with vigorous stirring of a 30 % solution of sodium nitrite, the optimum temperature of the reaction being 35 ^{o}C. The resulting diazo oxide was obtained in the form of its sodium salt by the addition of some sodium chloride.

3.5.4 Coupling Reaction

The coupling components, N, N-dimethylaniline, N, N-diethylaniline and dodecylpyridone were separately dissolved in acetic acid and cooled to 0 ^{o}C, by adding ice. Each of the diazonium salt solution previously prepared was added in over 30-40 minutes with vigorous stirring (Brent, 1987, Maradiya, 2010). The mixture was stirred for further 2-3

hours, under the temperature of 0-5 ^{o}C and the pH of the solution was adjusted to 4-5 using 10 % sodium hydroxide solution. The resulting product was then collected by filtration, washed with water and dried. The crude product was purified by recrystallizing it from ethanol.

3.6 Purification of the Dyes

The dyes prepared were purified through the same process of recrystallization as highlighted above for the intermediates. The heterocyclic disperse dyes required mixed solvent of acetic acid/DMF (9/1 solvent mixture) according to a procedure suggested by Alaa and Tarek (2006). The purity of each of the synthesized dyes was confirmed by TLC.

3.7 Percentage Yield of Dyes and Intermediates

The percentage yield of the synthesized dyes and intermediates were determined using the formula shown below (Yusuf, 2012).

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

where;

MP is the mass of the product

MMP is the molar mass of the product

MR is the mass of the reactant

MMR is the molar mass of the reactant

3.8 Characterization of the Synthesised Dyes and Intermediates.

The intermediates and the synthesized dyes were characterized using Gas chromatography-mass spectrometry (GC-MS), Fourier transform infra-red spectroscopy (FT-IR). Other tests carried out on the intermediates and dyes were the melting point determination and UV-visible spectrophotometry.

3.8.1 Melting Point Determination

The melting points of each dye and the aminothiophenes intermediates were determined by using Gallenkamp melting point apparatus. Small amount of each dye and intermediate was filled into a capillary tube each and placed into the apparatus; the melting point of each sample was obtained by consistently focussing on the apparatus as the apparatus gradually heated the samples. All the dyes and intermediates exhibited sharp and fairly well defined melting points characteristic of pure compounds.

3.8.2 Molar Extinction Coefficient

The molar extinction coefficient (Ɛ), which is a constant for each molecule at any given wavelength, represents the absorbance of a 1cm thickness of a medium containing 1 mole of the absorbing substance per litre (Giles, 1974). Ɛ was calculated using the relation:

$A = ƐCL$

where

Ɛ = Extinction coefficient

A = Absorbance at λ_{max}

C = Concentration of dye in mol/dm^3

L = Path length in cm

3.8.3 Determination of Visible Absorption Spectra

The visible absorption spectra were recorded on an Agilent CARY 300 UV-VISIBLE spectrophotometer from dye solutions in DMSO and methanol at a concentration of 1.5×10^{-5} mol/l as described by Yuh and Wei (2006).

3.8.4 FT-IR Determination

FT-IR spectra of the intermediates and the synthesized dyes were recorded on Agilent CARY 630 FT-IR spectrophotometer.

3.8.5 Gas Chromatography-Mass Spectrometry (GC-MS).

The structural elucidation of the synthesized dyes and intermediates were studied by the use of Agilent gas chromatography–mass spectrophotometer with model number 7890B GC System.

3.9 Application of Dyes

1 % stock solution of each dye was prepared, a liquor ratio of 50:1 was used, 2 % shade on weight of fabric (o.w.f) and 1 g of fabric each of polyester and chrome tanned leather. The volume required from each stock solution was calculated based on the formula;

$$V = \frac{P \times W}{C}$$

where:

P = percentage shade

W = weight of fabric

C = percentage concentration of stock solution.

3.9.1 Dyeing of polyester

For the polyester fabric, a carrier (phenol) and dispersing agent (anionic detergent) were used to facilitate the dyeing process. The fabric was wetted and thoroughly squeezed to remove excess water. It was then immersed into the bath at 40 °C and allowed to reach the boil within 15 minutes. Dyeing was carried out for one hour at a temperature of 100 °C with agitation. At the end of the dyeing process, the substrate was removed, squeezed and rinsed

thoroughly under running tap water and allowed to dry at room temperature (Giles, 1974., Nkeonye, 1987).

3.9.2 Dyeing of leather

The synthesised dyes were used in dyeing of chrome tanned leather. The standard method of dyeing leather was followed using the recipes below.

For neutralisation of chrome tanned leather:

I. 100 % water
II. 1 % sodium bicarbonate
III. Run for 15 minutes

For dyeing of chrome tanned leather:

i. 120 % of water (60 ^{o}C)
ii. 1 % of dye
iii. Run for 45 minutes

For dye fixation:

I. 0.1 % of formic acid
II. Run for 15 minutes

The pH of the chrome tanned leather was adjusted to 5.5 using 1 % sodium bicarbonate to neutralise the leather and thereafter washed thoroughly with distilled water. A solution of the dye sample (1 %) was made with distilled water using heating mantle and the temperature of the medium was raised to 60 ^{o}C, the leather sample was introduced into the dye bath solution and run for 45 minutes. 0.1 % of the formic acid was added to the dye bath and further run for 15 minutes in order to fix the dye on the substrate. The dyed leather was then removed from the bath and rinsed severally under running tap water and dried. This procedure was repeated for all the acid dyes on chromed tanned leather (Traubel and Eitel, 1977).

3.10 Determination of Dyebath Exhaustion

Dye uptake was determined by measuring the absorbance of diluted dyebath samples at the wavelength of the maximum absorption. The bath was sampled before and after dyeing. A 1 ml aliquot was taken from the bath and diluted in 20 ml acetone. This is to ensure that the absorbance falls within the readable range of 1.5. The percentage dyebath exhaustion (% E) for each substrate was calculated using the equation below (Jae-Hong Choi *et al.*, 2008; Ozan, 2011).

$$\% E = \frac{A_o - A_1}{A_o} \times 100$$

where A_o and A_1 are the absorbance at λ_{max} of the dyebath prior to dyeing and after dyeing respectively.

3.11 Assessment of Fastness Properties

3.11.1 Wash Fastness Test

The dyed samples were subjected to I.S.O.3 wash fastness test by the following procedures: The specimens were prepared by cutting the dyed fibres into 5 cm x 2 cm dimensions; they were then made into composites by stitching the test specimen made of the dyed sample placed in between white cotton of dimensions 10 cm x 4 cm. The composite was agitated in the solution made up of the following (Nkeonye, 1987):

Soap solution 5 g/l

Sodium carbonate 2 g/l

Liquor ratio 50:1

The washing was maintained at 50 °C for 45 minutes with continuous agitation. At the end of the washing test the composite specimen was removed, rinsed in cold water and the components separated and dried at room temperature. The change in colour of the dyed samples and the staining of adjacent undyed cloths were assessed using the appropriate grey scale.

3.11.2 Light Fastness Test

The dyed samples and blue wools 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 3 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 (Nunn, 1979).

Light fastness values for each material was obtained by comparing the degree of fading with that observed with Blue wool standard. Rating is given according to the Wool standard with which the dyed material fading is comparable.

3.12 Evaluation of the Antimicrobial Activity of Azo Dyes

3.12.1 Test organisms

The test organisms used for this analysis were clinical isolates of bacteria and fungi obtained from the Department of Microbiology, Ahmadu Bello University, Samaru Zaria, Nigeria. The isolates were: *Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, Candida krusei, Candida albicans and Aspergillus niger.*

3.12.2 Culture media

The culture media used for the analysis include Mueller Hinton Agar (MHA), Mueller Hinton Broth (MHB), Potato Dextrose Agar (PDA) and Nutrient Agar (NA).These media were used for Antimicrobial susceptibility testing viz: minimum inhibitory concentration

(MIC), and minimum bactericidal/fungicidal concentration (MBC/MFC). All the media were prepared according to manufacturer's instructions and sterilized by autoclaving at 121 °C for 15 minutes.

3.12.3 Determination of inhibitory activity (sensitivity test) of the synthesized dyes using agar well diffusion method

The standardized inocula of both the bacterial and fungal isolates were streaked on sterilized Mueller Hinton Agar and Potato Dextrose Agar plates, respectively with the aid of sterile swab sticks. Four wells were punched on each inoculated agar plate with a sterile cork borer. The wells were properly labelled according to different concentrations of the synthesized samples which were 100, 50, 25 and 12.5 mg/ml, respectively. Each well was filled up with 0.2 ml of the dye. The inoculated plates with the dyes were allowed to stay on the bench for about 1 hour; this is to enable the dye samples to diffuse on the agar. The plates were then incubated at 37 °C for 24 hour (plates of Mueller Hinton agar) while the plates of potato dextrose agar were incubated at room temperature (26-27 ^{o}C) for about 3-5 days.

At the end of the incubation period, the plates were observed for any evidence of inhibition which will appear as a clear zone that was completely devoid of growth around the wells (Zone of inhibition).The diameter of the zones were measured using a transparent ruler calibrated in millimetres.

3.12.4 Determination of minimum inhibitory concentration (MIC)

The minimum inhibitory concentrations of the synthesized samples were determined using tube dilution method with the Mueller Hinton Broth used as diluents. This is lowest concentration of the synthesized samples showing inhibition for each organism when the sample was tested during sensitivity test was serially diluted in the test tubes containing

Mueller Hinton Broth. The organisms were inoculated into each tube containing the broth and the synthesized samples. The inoculated tubes were then incubated at 37 °C for 24 hours.

At the end of the incubation period, the tubes were observed for the presence or absence of growth using turbidity as a criterion, the lowest concentration in the series without visible sign of growth (turbidity) was considered to be the minimum inhibitory concentration (MIC).

3.12.5 Determination of minimum Bactericidal/fungicidal concentration (MBC/MFC)

The result from the minimum inhibitory concentration (MIC) was used to determine the minimum Bactericidal/fungicidal concentration (MBC/MFC) of the synthesized sample. A sterilized wire loop was dipped into the test tubes that did not show turbidity (Clear) in the MIC test and a loopful was taken and streaked on a sterile nutrient agar plate. The plates were incubated at 37 °C for 18-24 hours.

At the end of incubation period, the plates were examined for the presence or absence of growth. This is to determine whether the antimicrobial effects of the synthesized samples are bacteriostatic/fungistatic or Bactericidal/fungicidal.

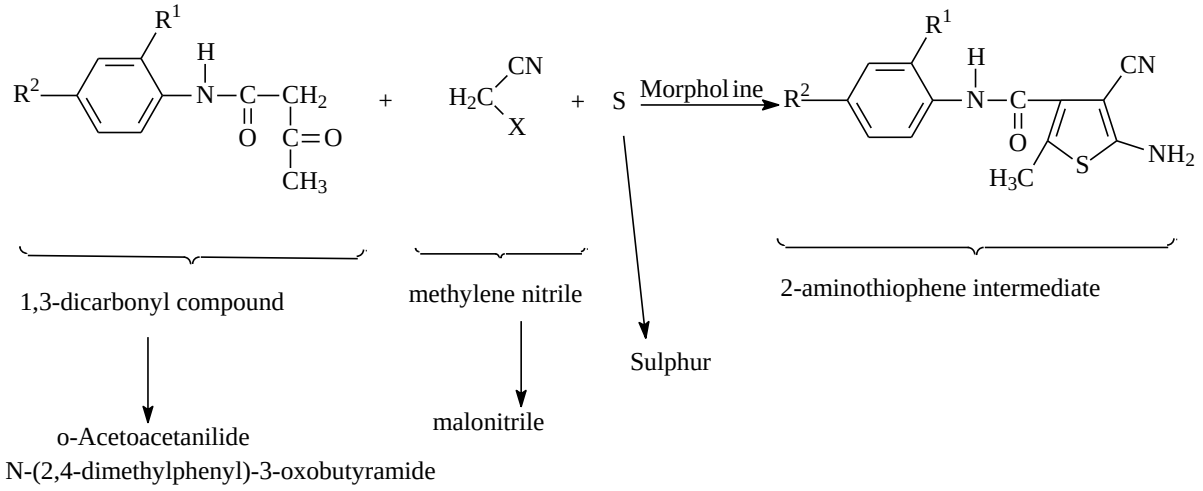
CHAPTER FOUR

4.0 RESULTS

4.1 Synthesis of 2-Aminothiophene Intermediates

4.1.1 Synthetic Route for the 2-Aminothiophene Intermediates

The synthetic route for the 2-aminothiophene intermediates used is as shown in scheme 4.1 below.



Scheme 4.1: Synthesis of aminothiophene intermediate

where R^1 = H, CH_3

R^2 = H, CH_3

X = CN

The synthesis of the 2-aminothiophenes intermediates 1 and 2 was achieved by using the Gewald's methodology reported in the work of Alaa and Tarek (2006) as outlined in scheme 4.1 above. This convenient methodology includes the condensation of the 1,3-dicarbonyl compounds (i.e. o-Acetoacetanilide and N-(2,4-dimethylphenyl)-3-oxobutyramide) with the activated methylene nitrile (i.e. malononitrile) in the presence of sulphur in ethanol.

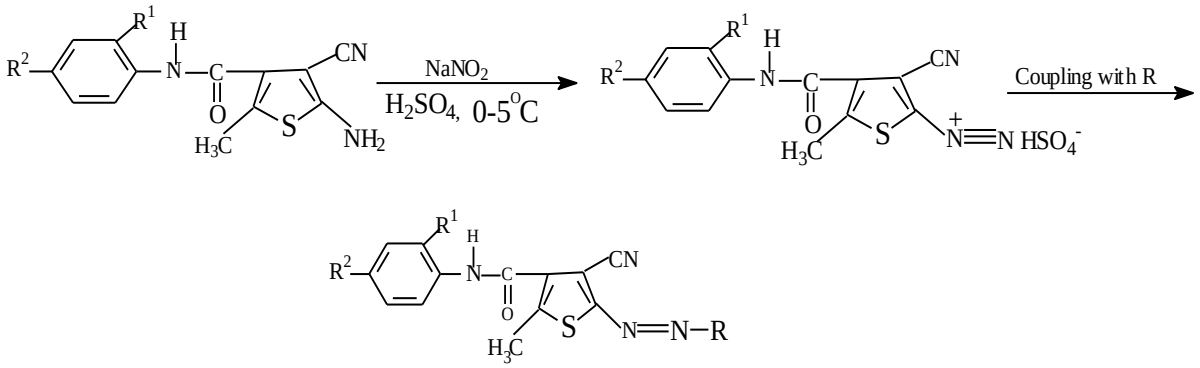
4.1.2 Physical Properties of 2-aminothiophene Intermediates

The molecular formula, molar mass, melting point, percentage yield and colour of the synthesized intermediates are presented in Table 4.1 below.

4.2 Synthesis of the Azo Dyes

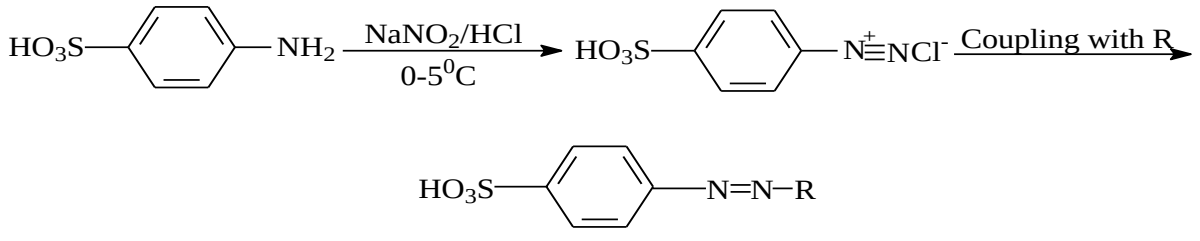
4.2.1 Synthetic route for the Synthesis of the Azo Dyes

The azo dyes were synthesized by diazotization of the intermediates 1 and 2 with nitrosyl sulphuric acid generated in-situ by the reaction of sodium nitrite and Concentrated sulphuric acid in an ice-bath and was coupled immediately with N,N-dimethylaniline, N,N-diethylaniline and Dodecyl pyridone as shown in the scheme 4.2-4.4 below:



Scheme 4.2: Diazotization and Coupling Reaction of 2-Aminothiophene intermediate 1 and 2 where R represent the coupling components viz: N,N-dimethylaniline, N,N-diethylaniline and Dodecyl pyridone.

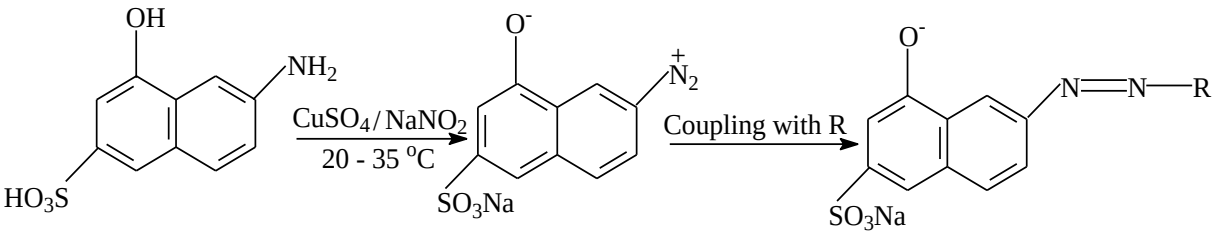
Sulphanilic acid and Gamma acid was diazotized via a direct method of diazotization with nitrosonium ion generated in-situ by reacting sodium nitrite and concentrated hydrochloric acid at a reduced temperature (0-5 ^{o}C) in an ice-bath to form the diazonium salt solution and immediately coupled with N,N-dimethylaniline, N,N-diethylaniline and Dodecyl pyridone as shown in the scheme 4.3 below.



Scheme 4.3: Diazotization and Coupling Reaction of Sulphanilic acid

where R represent the coupling components viz: N,N-dimethylaniline, N,N-diethylaniline and Dodecyl pyridone.

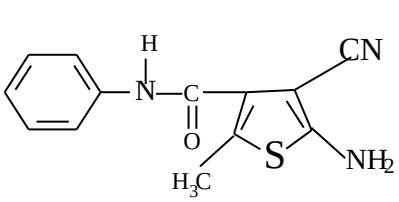
However Gamma acid was diazotized using a special technique by first adding copper sulphate solution to the solution of gamma acid in order to prevent the amine from decomposing into a quinone and thereafter, the direct method of diazotization with nitrosonium ion generated in-situ by reacting sodium nitrite and concentrated hydrochloric acid at a reduced temperature (0-5 ^{o}C) in an ice-bath to form the diazonium salt solution and immediately coupled with N,N-dimethylaniline, N,N-diethylaniline and Dodecyl pyridone as shown in the scheme 4.4 below.



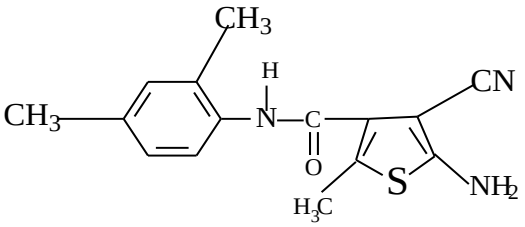
Gamma acid Diazo oxide

Scheme 4.4: Diazotization and Coupling Reaction of Gamma acid

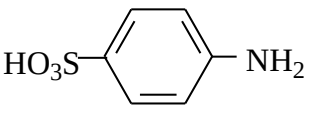
The structures of the intermediates that were diazotised are presented in Figure 4.1 below.



Intermediate 1

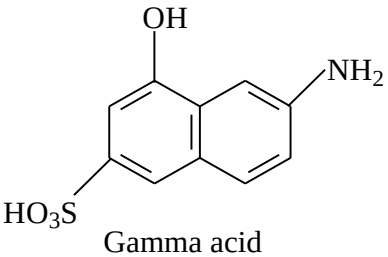


Intermediate 2



Sulphanilic acid

Intermediate 3

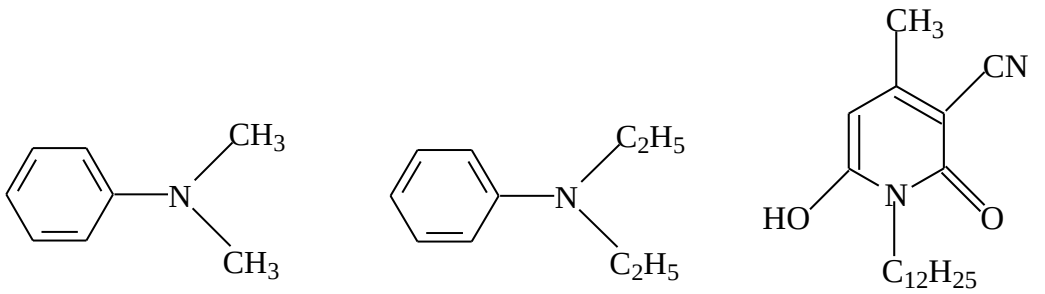


Gamma acid

Intermediate 4

Figure 4.1 Structures of the Intermediates that were Diazotised

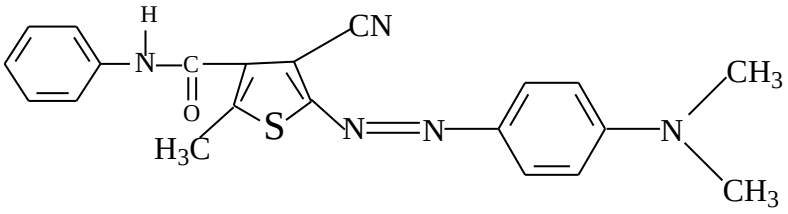
where R represent the coupling components viz: N,N-dimethylaniline, N,N-diethylaniline and Dodecyl pyridone as represented in Figure 4.2 below.



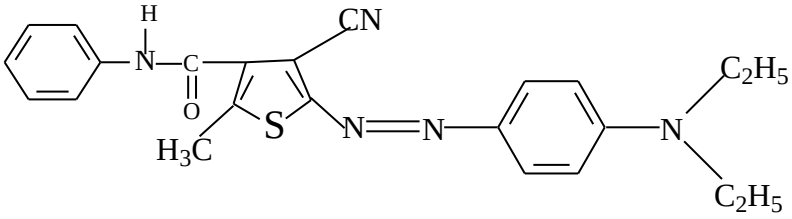
N, N-Dimethylaniline (a) N, N-Diethylaniline (b) Dodecylpyridone (c)

Figure 4.2: Structures of the Coupling components

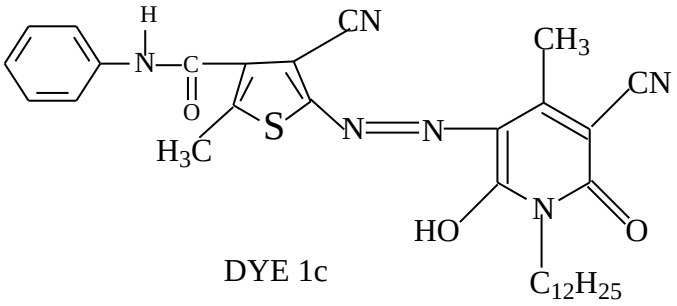
The structures of the synthesized dyes are presented in Figure 4.3 below;



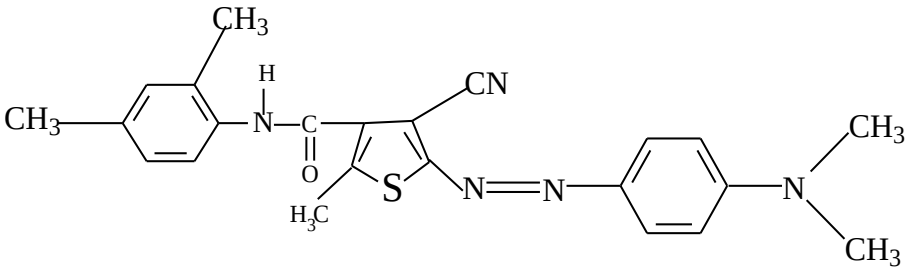
DYE 1a



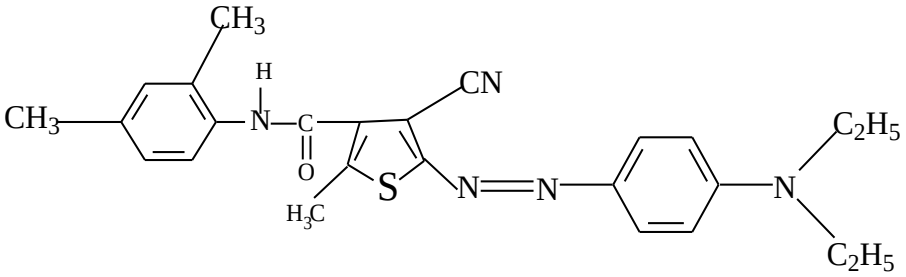
DYE 1b



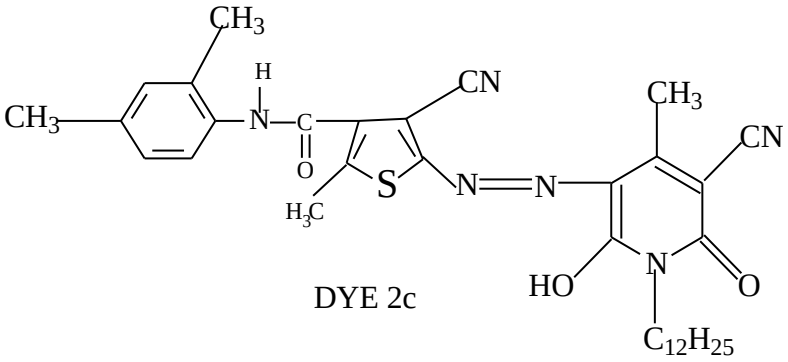
DYE 1c



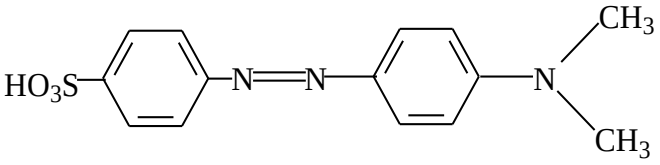
DYE 2a



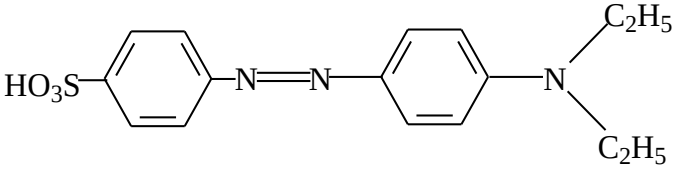
DYE 2b



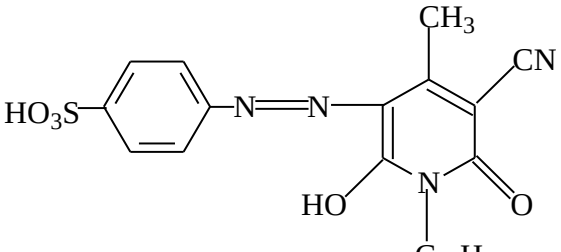
DYE 2c



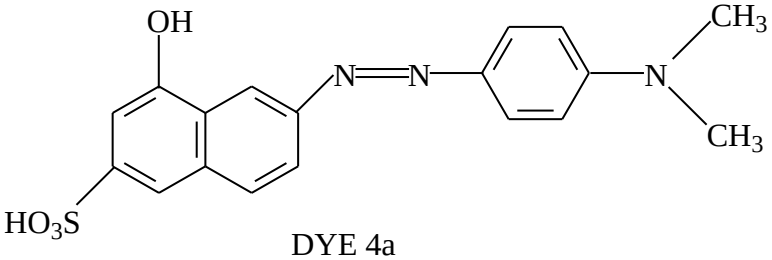
DYE 3a



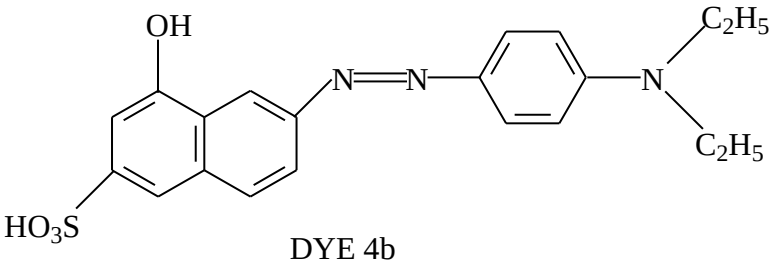
DYE 3b



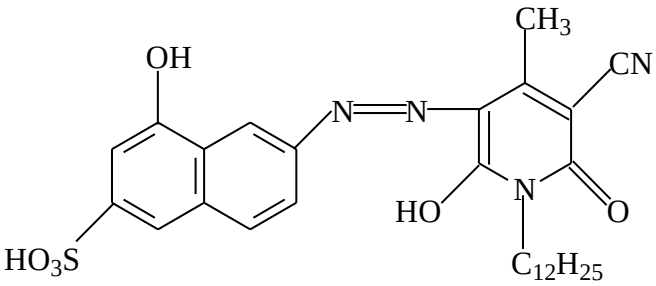
DYE 3c



DYE 4a



DYE 4b



DYE 4c

4.2.2 Physical Properties of the Synthesized Azo Dyes

The physical properties of the synthesized azo dyes are as shown in Table 4.2 below. This comprises of the molecular formula, molar mass, melting point, colour appearance of the dye crystals and percentage yield.

4.3 Characterization of the Synthesized Intermediates and Dyes

4.3.1 Visible absorption Spectroscopy of Dyes

The Visible absorption spectra of the dyes were measured in DMSO and methanol and their molar extinction coefficients calculated using their λmax in DMSO. The results are presented in Table 4.3 below.

4.3.2 Infra-Red Spectra of the Intermediates and Dyes

The FTIR peaks observed with the corresponding group present for the synthesized intermediates and dyes are shown in Table 4.4 below.

4.3.3 GC-MS of the Intermediates and Dyes

The GC-MS fragments of the synthesized 2-aminothiophene intermediates and some of the selected dyes is as shown in Table 4.5 below.

4.4 Antimicrobial Activity of the Synthesized Dyes

The antimicrobial activity of some of the synthesized dyes against six different pathogenic microorganisms are shown in Tables 4.6-4.8 below and this comprises of the Zone of Inhibition, minimum inhibitory concentration (MIC) and the minimum bactericidal/fungicidal concentration (MBC/MFC) of the test microorganisms against the synthesized dyes.

4.5 Dyeing of Polyester Fabric and Chrome Tanned Leather

4.5.1 Dyeing Exhaustion of the Synthesized Dyes

The results of the dye exhaustion of the synthesized dyes on polyester fabric and chrome tanned leather are shown in Table 4.9

4.5.2 Assessment of Fastness Properties to Washing and Light

4.5.2.1 Wash fastness.

The resistance of dyed materials to laundry treatment such as washing is referred to as washing fastness. The washing fastness test is considered very useful since dyed fabrics are subjected to various washing conditions during use. The general procedure recommended by the International Standard Organization, number 3 (ISO 3) was adopted and the results are shown in Table 4.10.

4.5.2.2: Light Fastness of the using 8 Blue Wool Standard.

The light fastness test results obtained using 8 Blue Wool Standards for each of the dyed substrates are shown in Table 4.11

Table 4.1: Physical Properties of 2-aminothiophene Intermediates

Intermediates	Molecular formula	Molecular weight (g/mol)	Melting point	Percentage yield	Appearance of Intermediates	R_f values
1	$C_{13}H_{11}N_3OS$	257	201-208	48	Brown	0.46
2	$C_{15}H_{15}N_3OS$	285	165-167	53	Dark brown	0.40

Table 4.2: Physical Properties of the synthesized azo dyes

Dye	Molecular formula	Molecular weight (g/mol)	Melting point (^oC)	Percentage yield (%)	Retention factor (R_f)	Appearance of dye crystals
Dye 1a	$C_{21}H_{19}N_5OS$	389	204-210	57.82	0.48	Magenta
Dye 1b	$C_{23}H_{23}N_5OS$	417	209-213	43.00	0.43	Ash
Dye 1c	$C_{32}H_{38}N_6O_3S$	586	198-206	60.40	0.56	Brown
Dye 2a	$C_{23}H_{23}N_5OS$	417	159-163	40.15	0.51	Maroon
Dye 2b	$C_{25}H_{27}N_5OS$	445	160-165	38.10	0.47	Maroon
Dye 2c	$C_{34}H_{42}N_6O_3S$	614	168-173	47.04	0.58	Brown
Dye 3a	$C_{14}H_{15}N_3O_3S$	305	184-190	80.26	0.55	Red
Dye 3b	$C_{16}H_{19}N_3O_3S$	333	180-187	69.22	0.53	Purple
Dye 3c	$C_{25}H_{35}N_4O_5S$	503	164-168	73.00	0.63	Cream
Dye 4a	$C_{16}H_{17}N_3O_4S$	371	171-176	66.69	0.49	Green
Dye 4b	$C_{18}H_{21}N_3O_4S$	399	174-180	63.12	0.67	Yellow
Dye 4c	$C_{27}H_{36}N_4O_6S$	568	161-164	69.00	0.82	Brown

Table 4.3: Visible absorption Spectroscopy of Dyes

Dye No	ε_{max} (in DMSO) ($Lmol^{-1}cm^{-1}$)	DMSO λ_{max} (nm)	Methanol λ_{max} (nm)
Dye 1a	27133.33	554	464
Dye 1b	20866.67	524	461
Dye 1c	36400.00	569	529
Dye 2a	31066.67	564	513
Dye 2b	29133.33	541	536
Dye 2c	19933.33	529	492
Dye 3a	41333.33	431	420
Dye 3b	28266.67	440	433
Dye 3c	20333.33	439	453
Dye 4a	47333.33	444	445
Dye 4b	19566.67	448	449
Dye 4c	42066.67	454	446

Table 4.4: The Infra-Red Spectra of the Intermediates and Dyes

Intermediates/Dyes	Vibrational frequencies (cm^{-1})
Intermediate 1	3421.7, 3276.3 (NH), 2199.1 (CN), 1695.9, 1662.4 (C=O)
Intermediate 2	3354.6, 3317.3, 3198.1 (NH), 2206.6 (CN), 1647.5, 1602.8 (C=O)
Dye 1a	3302.4, 3350.9, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2959.9, 2870.1 (C-H)
Dye 1b	3302.4, 3347.1, 3459.0 (NH), 2214.0 (CN), 1695.9, 1662.4, 1602.8 (C=O), 1453.7, 1505.8 (N=N), 2873.8, 2967.0 (C-H)
Dye 1c	3429.2 (NH), 2273.7 (CN), 1613.9, 1722.0 (C=O), 1509.6, 1569.2 (N=N), 2944.6 (C-H)
Dye 2a	3426.4 (NH), 2273.7 (CN), 1613.9, 1722.0 (C=O), 1509.6, 1569.2 (N=N), 2944.6, 2788.0 (C-H)
Dye 2b	3313.6 (NH), 2214.0 (CN), 1707.1, 1651.2 (C=O), 1490.9, 1416.4 (N=N), 2922.2 (C-H)
Dye 2c	3298.7 (NH), 2214.0 (CN), 1651.2 (C=O), 1490.9, 1543.1 (N=N), 2847.7, 2918.5 (C-H)
Dye 3a	3388.2 (NH), 2836.5 (C-H), 1487.2, 1595.3, 1543.1 (N=N)
Dye 3b	3473.9, 3552.2 (NH), 2993.1 (C-H), 1543.1, 1595.3, 1431.3 (N=N)
Dye 3c	3317.3 (NH), 2847.7, 2918.5, 2959.5 (C-H), 2281.1 (CN), 1699.7, 1632.6 (C=O), 1509.6, 1569.2, 1442.5 (N=N)
Dye 4a	3399.3 (OH), 2933.4 (C-H), 1226.3, 1177.8 (C-N), 1509.6, 1599.0, 1554.3 (N=N)
Dye 4b	3309.9 (OH), 2922.2 (C-H), 1114.5, 1271.0 (C-N), 1490.9, 1438.8, 1595.3 (N=N)
Dye 4c	3332.2 (OH), 2851.4, 2914.8 (C-H), 2221.5 (CN), 1640.0 (C=O), 1509.6, 1423.8 (N=N)

Table 4.5: GC-MS of the Intermediates and Dyes

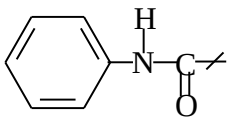
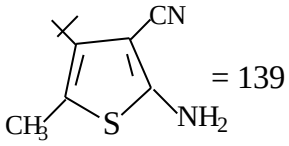
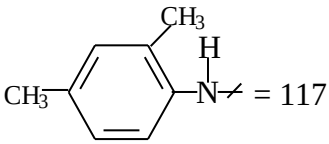
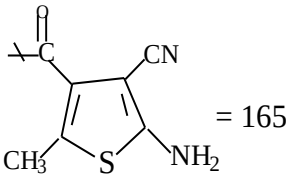
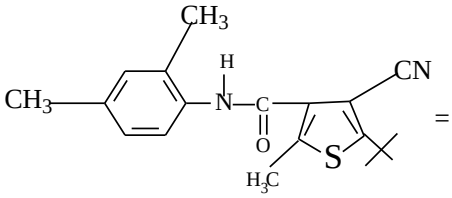
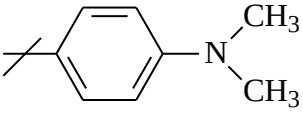
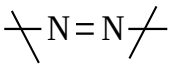
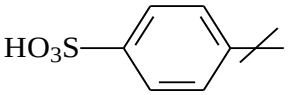
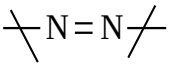
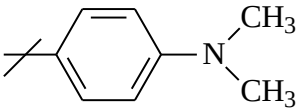
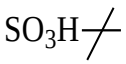
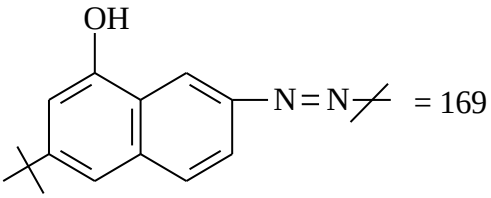
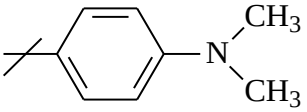
Intermediate/Dyes	Mass (m/z)
Intermediate 1	 =123,  = 139
Intermediate 2	 = 117,  = 165
Dye 2a	 = 273,  = 113,  = 29
Dye 3a	 = 153,  = 29,  = 125
Dye 4a	 = 85,  = 169,  = 113.1

Table 4.6: Zone of Inhibition (mm) of the Test Organisms by Synthesized Dyes

Test Organism	Dye 1a	Dye 1b	Dye 1c	Dye 2a	Dye 2b	Dye 2c	Dye 3a	Dye 3b	Dye 3c	Dye 4a	Dye 4b	Dye 4c	Spar flo	Flu co
Staphylococcus aureus	23	27	29	23	27	34	16	19	26	13	21	24	37	-
Escherichia coli	26	25	28	21	23	29	18	24	21	17	19	21	35	-
Pseudomonas aeruginosa	28	26	26	26	28	33	15	17	25	20	0	10	35	-
Candida albicans	20	20	25	21	16	27	19	0	03	15	05	09	-	32
Candida krusei	19	16	23	25	20	23	12	0	14	18	10	16	-	34
Aspergillus niger	14	21	17	22	18	20	20	16	19	17	14	19	-	35

Key:

Sparflo: Sparfloxacin = 5µg/ml (Positive control drug for bacteria)

Fluco: Fluconazole = 5µg/ml (positive control drug for fungi)

Table 4.7: Minimum Inhibitory Concentration (MIC) mg/ml of the Synthesized Dyes against Test Microorganisms

Test Organism	Dye 1a	Dye 1b	Dye 1c	Dye 2a	Dye 2b	Dye 2c	Dye 3a	Dye 3b	Dye 3c	Dye 4a	Dye 4b	Dye 4c
Staphylococcus aureus	12.5	50	25	25	25	12.5	50	100	12.5	50	–	25
Escherichia coli	25	50	25	50	100	50	50	50	25	50	100	50
Pseudomonas aeruginosa	50	25	25	25	12.5	25	50	50	50	50	ND	–
Candida albicans	25	50	12.5	25	25	12.5	25	ND	–	25	–	100
Candida krusei	12.5	25	50	50	25	100	50	ND	50	50	–	50
Aspergillus niger	25	25	50	50	25	25	100	25	50	50	25	50

Table 4.8: Minimum Bactericidal/Fungicidal Concentration (MBC/MFC) mg/ml of the Synthesized Dyes against Test Microorganisms

Test Organism	Dye 1a	Dye 1b	Dye 1c	Dye 2a	Dye 2b	Dye 2c	Dye 3a	Dye 3b	Dye 3c	Dye 4a	Dye 4b	Dye 4c
Staphylococcus aureus	12.5	50	25	50	25	12.5	100	100	12.5	50	─	25
Escherichia coli	50	50	25	50	100	50	50	50	25	100	100	50
Pseudomonas aeruginosa	50	25	25	50	12.5	25	100	50	50	50	ND	─
Candida albicans	50	50	12.5	25	25	12.5	50	ND	─	50	─	100
Candida krusei	25	25	50	50	25	100	100	ND	50	100	─	50
Aspergillus niger	50	25	50	100	25	25	100	25	50	50	25	50

Key:

ND = No detection

─ = No activity

Table 4.9: Dye Exhaustion on Polyester Fabric and Chrome Tanned Leather

Dye No.	% Exhaustion on Polyester Fibre	% Exhaustion on Chrome Tanned Leather
1a	75	-
1b	70	-
1c	78	-
2a	60	-
2b	68	-
2c	73	-
3a	-	80
3b	-	85
3c	-	84
4a	-	82
4b		86
4c		87

Table 4.10: Wash Fastness of the Synthesized Dyes on polyester fabric and chrome tanned leather Using ISO 3 Standard.

Dye No.	Change in Colour		Staining of Adjacent Fabric		Colour on Substrate
	Polyester Fibre	Chrome tanned Leather	Polyester Fabric	Chrome tanned Leather	
1a	5	-	4-5	-	Deep pink
1b	4	-	4	-	Light purple
1c	4-5	-	4-5	-	Brown
2a	4-5	-	4-5	-	Light purple
2b	4	-	4	-	Violet
2c	5	-	5	-	Brown
3a	-	3-4	-	3-4	Golden yellow
3b	-	4-5	-	4-5	Orange
3c	-	5	-	4-5	Grey
4a	-	3	-	3-4	Brown
4b	-	4	-	4	Coffee brown
4c	-	4-5	-	4	Deep purple

Change in shade

5 = Excellent

4 = Very good

3 = Good

2 = fair

1 = poor

Staining

5 = no staining

4 = very slight staining

3 = moderate staining

2 = significant staining

1 = deep staining

Table 4.11: Light Fastness of the Synthesized Dyes on polyester fabric and chrome tanned leather

Dye No.	Polyester Fabric	Chrome Tanned Leather
1a	6	_
1b	5	_
1c	5	_
2a	6	_
2b	5	_
2c	4	_
3a	_	5
3b	_	5
3c	_	4
4a	_	5
4b	_	4
4c	_	4

Fastness grade	Degree of fading	Fastness grade	Degree of fading
8	none	4	appreciable
7	very slight	3	significant
6	slight	2	extensive
5	moderate	1	very extensive

CHAPTER FIVE

5.0 DISCUSSION

5.1 Synthesis and Physical Properties of 2-aminothiophene Intermediate

The molecular formula, molecular weight, melting point, percentage yield, appearance of the dye crystals and retention factor of the synthesized 2-aminothiophene intermediates were presented in Table 4.1. The synthesis of the 2-aminothiophene intermediates 1 and 2 were achieved by using the Gewald's method as outlined in Scheme 4.1. This was prepared by heating the required mole of 1,3-dicarbonyl compound (i.e. o-Acetoacetanilide and N-(2,4-dimethylphenyl)-3-oxobutyramide) with the required mole of activated α-methylene nitrile (i.e. malononitrile) in the presence of sulphur in ethanol.

The colours of the heterocyclic diazo components are brown and dark brown for the intermediates 1 and 2, respectively. The molecular mass of the intermediates is 257 and 285 g/mol while the melting point ranges from 165 to 208 °C as shown in the Table 4.1 above. The yield of the 2-aminothiophene intermediates can also be described as fair (48) to good (53).This is not surprising in view of the result from previous and similar works such as Sabnis *et al*. (1999) who reported that 1, 3-dicarbonyl compound generally pose a problem of low yield and difficult purification process when compared to other ketones and aldehydes. One of the methods mentioned however, as a way of overcoming this is a prolonged reaction time. This was also supported by Jack (2005), who reported that generally ketones starting materials produced far poorer result than aldehydes. They suggested that the use of a precondensed Knoevenagel intermediate may be preferred. Equally, Victor *et al*. (2006) reported that aryl ketones appear generally unreactive in the direct one-spot Gewald synthesis. The R_f values of the synthesized aminothiophenes in hexane : ethyl acetate as eluent in the ratio of 1:1 indicates that the intermediates gave one spot each which means that the samples are pure.

5.2 Synthesis and Physical Properties of the Azo Dyes

The physical properties of the synthesized azo dyes were presented in the Table 4.2 above. These properties consist of their molecular formula, molecular weight, melting point, percentage yield, the retention factor and the appearance of the synthesized dye crystals.

The molecular weight of the compounds ranges from the highest 614 which was obtained for Dye 2c to the lowest 305 which was observed in Dye 3a. All the purified dyes exhibited fairly well-defined melting points characteristics of a pure compound as shown above, whilst it would be unwise to attempt to explain in detail their relative value because of the complex dependence of the melting points on a number of factors (e.g. polarity, size geometry and interaction); however, a few general trends can be accounted for. The dyes from low-melting diazo components tended to have low melting points themselves and the factors determining high melting points were generally observed in the dyes from high-melting heteroaryl amines as shown in Table 4.2 above. Thienyl-2-azo dyes with 3-cyano groups had higher melting points than their analogues with alkyl esters, which as Hallas and Towns (1996a and 1996b) had earlier observed, may be as result of increased polarity and/or the rod like shape of the cyano group being more conducive to efficient packing in the crystal structure. For instance, dyes 1a, 1b and 1c had melting points of 204-210 ^{o}C, 209-213 ^{o}C and 198-206 ^{o}C respectively. These figures are close in magnitude to that of the aminothiophene intermediate 1 which had a melting point of 201-208 ^{o}C. A similar trend was observed from intermediate 2 which had a melting point of 165-167 ^{o}C with the corresponding dye series dye 2a (159-163 ^{o}C), dye 2b (160-165 ^{o}C) and dye 2c with the melting point of 168-173 ^{o}C, respectively. The entire compounds were synthesized in good (57.82 %) to excellent yield (80.26 %) except for dyes 1b, 2a, 2b and dye 2c where-in arbitrarily low yields of 43.00 %, 40.15 %, 38.10 % and 47.04 % were observed, respectively. The low yield of these dyes could be attributed to the 1, 3-dicarbonyl compound used (Sabnis *et al*. 1999). The TLC spotting was done in order to monitor the progress of the reaction and to confirm the purity

level of the products obtained. The retention factor (R*f*) of all the dyes gave one spot each, indicating the purities of the dyes. Although, the solvent systems are the same for all the compounds but in varying ratio, the eluting ratio varies depending on the polarity disparity of the synthesized dyes. The dye crystals obtained gave different colours ranging from yellow to deep red.

5.3 Characterization of the Synthesized Intermediates and Dyes

5.3.1 Visible absorption spectroscopy of dyes in DMSO and Methanol

Table 4.3 shows the λmax (wavelength of maximum absorption) of the synthesized dyes. Most of the dyes showed strong and broad absorption in the visible region, which shows the presence of colour imparting chromophores which are responsible for the hues. Hue is the predominant colour transmitted by an organic compound when the complementary colour contained in the light passing it has been absorbed. The colour of the azo dyes depends on the nature of both the diazo and the coupling components (Griffith, 1984).

The wavelength of maximum absorption (ʎmax) of the dyes ranges from 431-569 nm in DMSO to 420-536 nm in methanol. From the results in Table 4.3, dye 1a which was synthesized using 2-aminothiophene intermediate 1 as diazo component and coupled with N,N-dimethylaniline absorbed at 554 nm in DMSO, dye 2a which was obtained using 2-aminothiophenes intermediate 2 as diazo component and N,N-dimethylaniline as coupling component absorbed at 564 nm and similarly, dye 3a and 4a obtained from sulphanilic acid and gamma acid as diazo components and using N,N-dimethylaniline as coupling component absorbed at 431 nm and 444 nm, respectively. Thus dye 2a is more bathochromic than dyes 1a, 3a and 4a as it absorbed at a longer wavelength. Thus, dyes that absorbed at a lower wavelength indicate that they require higher energy for excitation (Marini and Munoz, 2010).

Dye 1b which was obtained from heterocyclic diazo compound (i.e. aminothiophene intermediate 1) and coupled with N,N-diethylaniline absorbed at 524 nm in DMSO, dye 2b

synthesized from heterocyclic diazo component (i.e. aminothiophene intermediate 2), and coupled with N, N-diethylaniline absorbed at a wavelength of 541 nm while dyes 3b and 4b obtained from sulphanilic acid and gamma acid as the diazo components with the same N, N-diethylaniline as the coupling component absorbed at different wavelengths of 440 and 448 nm in DMSO, respectively. Thus dye 2b is more bathochromic than 1b, 3b and 4b by a wavelength of 17 nm, 101 nm and 93 nm, respectively. This marked bathochromic shift is not surprising for a dye molecule containing heterocyclic ring system as compared to the benzenoid counterparts. In a study carried out by Kyriaki and Eforia (2002) on the effect of substituents, it was observed for instance that a dye derived from aniline and 2-methoxy-5-acetylamino-N,N-di-β-acetoxyethyaniline is deep yellow with λmax of 428 nm; replacement of the phenyl moiety by the 6-nitrobenzothiazole residue results in a bathochromic shift of 148.5 nm. A large bathochromic shift of 116.5 nm is observed even when the benzothiazole residue is substituted with the electron donor methoxy group.

Particularly, derivatives of thiophene, thiazole and isothiazole, i.e. heterocyclic system containing sulphur as the heteroatom, represent a very electronegative diazo component, and consequently have a huge bathochromic effect compared with the corresponding benzenoid compounds.

The introduction of the cyano group as an electron–withdrawing substituent unto the thiophene ring produces a bathochromic shift of the absorption band in dye 1a, 2a, 1b and 2b as compared to dye 3a, 4a, 3b and 4b which produces a hypsochromic shift as a result of the replacement of the five membered ring sulphur heterocyclic diazo component with their six-membered analogues as the diazo component of their respective azo dyes. These bathochromic shifts afforded by five membered ring sulphur heterocycles have been mentioned by several authors (Griffiths, 1981 and 1982; Egli, 1991; Towns, 1999), indicating that these systems are useful in providing blue to greenish blue dyes. The origin of the large shift peculiar to this heterocyclic system could not be explained only in terms of greater

stabilization of the excited state, but probably is correlated with the increased diene character of the heterocycles (Peters and Gbadamosi, 1992).

Most of the shifts in wavelength of maximum absorption observed were bathochromic for majority of the dyes where measurements were done in solvent of higher polarity. The wavelengths of maximum absorption values shifted to longer wavelengths when the solvent is changed from methanol to dimethylsulphoxide (DMSO) e.g. dye 1a, 1b and 1c absorbs at wavelengths of 464 nm, 461 nm and 529 nm in methanol and 554 nm, 524 nm and 569 nm in DMSO, respectively. Likewise, dye 2a, 2b and 2c absorbed at 513 nm, 536 nm and 492 nm in methanol, while in DMSO, they absorbed at the wavelengths of 564 nm, 541 nm and 529 nm, respectively.

Solvent polarity effects on visible absorption band of dyes have been thoroughly studied and well documented in literature (Venkataraman, 1972). The literature reported that $\pi \rightarrow \pi^*$ transition exhibits bathochromic effect when the polarity of the solvent is increased while $n \rightarrow \pi^*$ transition shows hypsochromic effect with decrease in solvent polarity. This is a clear indication that in this study, the visible band is due to $\pi \rightarrow \pi^*$ transition since a positive solvatochromism occurred in some of the dyes and $n \rightarrow \pi^*$ transition since a negative solvatochromism also occurred in some of the dyes.

The molar extinction coefficient was calculated based on the concentrations of the dyes in DMSO 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 was observed that dyes (3a, 4a, and 4c) possessing high molar extinction coefficient appears brighter on the substrate. 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 (Mclaren, 1983).

5.3.2 The Infra-Red Spectra of the Intermediates and Dyes

The results of the infra-red analysis carried out for the aminothiophene intermediates and all the synthesized dyes were presented in Table 4.4 above. From the results, the IR spectra of aminothiophene intermediates 1 and 2 showed absorption peaks in the range 2199.1-2206.6 cm^{-1} due to the presence of the cyano group. The amino group absorption for the two intermediates appeared in the range 3198-3421.7 cm^{-1} while the carbonyl absorption is seen in the range 1602-1695 cm^{-1}.

As seen from the IR spectra of the synthesized dyes in Table 4.4, all the dyes gave absorption peaks due to azo group N=N stretching vibration at the range of 1416.4-1599.0 cm^{-1} and the C-H stretching vibration band at 2993.1-2788.0 cm^{-1}. An absorption peak in the region 2281.1-2214.0 cm^{-1} due to V_{CN} was observed for the synthesized azo dyes 1a, 1b, 1c, 2a, 2b, 2c, 3c and 4c, NH stretching vibration was observed at the frequency range of 3552.2-3302.4 cm^{-1} for synthesized azo dyes 1a, 1b, 1c, 2a, 2b, 2c, 3a, 3b, and 3c. The IR spectra of some of the synthesized azo dyes also showed an absorption peak in the region of 1722.0-1602.8 cm^{-1}, attributed to C=O stretching vibration for azo dyes 1a, 1b, 1c, 2a, 2b, 2c, 3c and 4c respectively. An absorption peak in the region 3399.3-3309.9 cm^{-1} due to OH stretching vibration was observed for azo dyes 4a, 4b and 4c, while the observed peak in the region 1271.0-1114.5 cm^{-1} attributed to C-N bending vibration was seen in the synthesized azo dyes 4a and 4b as outlined in Table 4.4.

5.3.3 GC-MS Spectra of the Synthesized Intermediates and Dyes

The results in Table 4.5 showed the fragmentation of the intermediates, dyes and their respective mass (m/z). The mass spectra of the intermediates 1 and 2 are fully consistent with the assigned structures: In most cases, intense molecular ion peaks were observed. Thus intermediates 1 and 2 showed intense molecular ion peaks at m/z 259 ± 2 and 282 ± 3, consistent with the molecular formulae $C_{13}H_{11}N_3OS$ and $C_{15}H_{15}N_3OS$ respectively. The

molecular ion of the intermediate 1 underwent fragmentations to produce peaks at m/z 123 and 139 corresponding to its molecular mass. While the intermediate 2 underwent fragmentation to produce peaks at m/z 117 and 165, respectively.

Dyes 2a, 3a and 4a showed molecular ion peaks at m/z 414.0±3, 308.0±3 and 366.4±5, respectively which are consistent with the molecular formula of dye 2a, 3a and 4a. The molecular ion in dye 2a underwent fragmentation to produce peaks at 273.0±4, 113.0±7 and 29.0±1. Dye 3a also underwent fragmentation to produce peaks at 153.0±4, 29.0±1 and 125.0±5, while the molecular ion peak in dye 4a underwent fragmentation to produce peaks at m/z 85.0±4, 169.1±1 and 113.1±7, respectively. Thus, the observed fragmentations for the dye 2a, 3a and 4a correspond to the respective molecular weight of the dyes.

Thus, the slight difference in numerical value of the molecular weight of the dyes can be attributed to certain elements with high isotopic abundance (Khoptar, 2008).

5.4 Antimicrobial Screening of the Synthesized Dyes

The Antimicrobial activities of the synthesized dyes were studied against six different microbes of which three were bacteria (*Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa)* and the other three were fungi (i.e. *Candida albicans, Candida krusei and Aspergillus niger)* by measuring the zone of inhibition on agar plates. It was observed from these results that dyes (1a-4c) had antimicrobial activity against different bacteria and fungi species, which are also known as human pathogenic microbes.

The compounds possess moderate to good activity against all tested microbes in comparison with standard drug as presented in Table 4.6 above. The zone of inhibition ranges from 03-34 mm except for dye 3b which has no effect on *Candida albicans, Candida krusei* and dye 4b which has no activity against *Pseudomonas aeruginosa*. It was observed that within the synthesized azo dyes, the highest zone of inhibition was recorded in dye 2c against *Staphylococcus aureus* i.e. 34 mm, which is close to that of the standard drug.

The result from Table 4.6 shows that all the synthesized heterocyclic disperse dyes possess higher inhibitory effect against the test organisms as compared to the conventional azobenzene dyes which is in consonance with the work of Himani *et al.* (2010).

The MIC values of all the test compounds ranged from 12.5 to 100 mg/ml as presented in Table 4.7. The synthesized dye 1a, 1c, 2b, 2c and 3c showed significant inhibition at MIC 12.5 mg/ml against *Pseudomonas aureginosa, Staphylococcus aureus, Candida albicans* and *Candida krusei*. This high MIC values afforded by the heterocyclic disperse dyes against the test microorganisms correlate with the work of Swati *et al*. (2011).

The effect of the synthesized dyes on the MIC for the test microorganisms correlate with the report of Emeruwa (2012), that microorganisms varied widely in the degree of their susceptibility. Antimicrobial agents with a low activity against an organism have a high MIC while a highly active antimicrobial agent gives a low MIC. *Staphylococcus aureus* is known to play a significant role in skin diseases including superficial and deep follicular lesion (Srinivasan *et al.,* 2001). So the strong activity of some of these dyes against *Staphylococcus aureus* indicates that the dye can be effective against skin infections. It is important to note that the strong activity of the dyes against *Candida albicans* and *Candida krusei* indicates that the dyes can be used as a topical anti-fungal agent. The synthesized dyes can also be used for the treatment of skin infections (Thomas, *1979*).

As low as MIC value of 12.5 mg/ml and MBC/MFC value of 12.5 mg/ml of the synthesized dyes as presented in Table 4.8, had activity against *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Candida albicans*; this shows the strength of activity of the dyes against the test microorganisms and that most of these dyes are not only bacteriostatic/fungistatic but were also Bactericidal/fungicidal in their action.

Most of the synthesized dyes having heterocyclic system containing thiophene ring possess enhanced antimicrobial activity. This strong antimicrobial activity may be due to attachment of the thiophene moieties which may further be attributed to greater extent in the

alteration of the chemical structure and presence of the cyano group, which is in agreement with the work of Shridhar *et al.,* (2011).

Most of the synthesized azo dyes had high activity against *Staphylococcus aureus, Pseudomonas aeruginosa, Candida albicans* and *Candida krusei,* so it can be used as antibacterial and antifungal agent on the finishing of various fabrics for manufacture of fabric for white coat and laboratory coat worn by Medical Doctors and Laboratarians, respectively. This antimicrobial finishing properties exhibited by some of these dyes have been reported in the work of Ma, (2005) and Mohammad *et al.* (2010).

5.5 Dyeing of Polyester Fabric and Chrome Tanned Leather

5.5.1 Dye Exhaustion on Polyester Fibre and Chrome Tanned Leather

The results of the percentage exhaustion of the synthesized dyes on polyester fabric and chrome tanned leather were presented in Table 4.9 above. From the results summarised in Table 4.9, dyes 1a, 1b, 1c, 2a, 2b and 2c applied on polyester fabric have percentage exhaustion of 75 %, 70 %, 78 %, 60 %, 68 % and 73 %, respectively while dyes 3a, 3b, 3c, 4a, 4b and 4c applied on chrome tanned leather have percentage exhaustion of 80 %, 85 %, 84 %, 82 %, 86 % and 87 %, respectively. The levels of exhaustion ranged from high to moderate upon application with wide variation of colour yield obtained. The acid dyes on chrome tanned leather gave high exhaustion as compared to the heterocyclic disperse dyes applied on polyester fibre. This is probably due to the solubility of the dyes, high rate of diffusion of the dye molecules into the fibre and greater accessibility of the pore structure in chrome tanned leather (Convington *et al.,* 2005)

5.5.2 Wash Fastness of the Synthesized Dyes on Polyester Fibre and Chrome Tanned Leather using ISO 3 Standard.

The Table 4.10 shows that the wash fastness of the heterocyclic disperse dyes 1a, 1b, 1c, 2a, 2b and 2c applied at 2 % depth on polyester fabric gave a better wash fastness as compared to the acid dyes 3a, 3b, 3c, 4a, 4b and 4c which was applied on chrome tanned leather. These dyes gave deep pink to deep purple hues with brighter and deeper shades, high tinctorial strength and excellent levelness on the fibres. The variation in the shade of the dyed polyester fibre and chrome tanned leather results from alteration in the diazo and coupling components. Thus from Table 10, all the heterocyclic disperse dyes exhibited good to excellent fastness to washing on polyester fabric while the acid dyes gave fair to very good fastness to washing on chrome tanned leather, respectively.

The remarkable degree of levelness and brightness after washing indicate good penetration and excellent affinity of the dyes to the fibres. In addition, the result obtained showed that the dyed polyester fabrics have excellent fastness level to washing as compared to the dyed chrome tanned leather which may be due to the presence of solubilising group, which affect solubility and washing ability of the dye-out of the dyed substrate (Gregory, *et al.,* 2005).

The reaction of the acid dyes with leather is a chemical reaction and is ruled by the laws of chemical reactivity (Lan, *et al.,* 2000; Ramasami, 2001). This reaction is a heterogeneous one between a soluble compound and an insoluble substrate. The desired result is a surface fibre reaction that is uniform in colour regardless of whether the colour is deeply tinted or very faint. And this is necessary in spite of the fact that the substrate is quite often very uneven in structure (Convington, *et al.,* 2005). Also, for the leather, the fastness properties depend on the type of tannage, the presence of chemical active substances in the float, surface active agents (Gregory, *et al.,* 2005; Li, *et al.,* 2006) on the fibre surface, salt content of the float etc. For the dye, it depends on the structure of the dyestuff or mixtures

thereof, their sensitivity to any of the dyeing conditions such as temperature, acidity, salt concentration (ionic strength) and so on.

5.5.3 Light Fastness of the Synthesized Dyes on Polyester Fibre and Chrome Tanned Leather using 8 Blue Wool Standards.

The light fastness ratings of the dyed polyester fabric and chrome tanned leather were presented in Table 4.11 and the results indicate moderate to very good light fastness. In attempting to trace the relationship between chemical structure and light fastness, it was observed by Maradiya (2010), that there is no absolute value for the light fastness of a dye. The rating obtained for a given colourant for any fading test depends on many factors most of which are: concentration and/or degree of aggregation of dye within the fabric, nature of the fabric in which the dye is dispersed; the characteristics of the incident radiation, molecular structure of the dye and substantivity. However, the light fastness observed for both the synthesized heterocyclic disperse dyes on polyester fabric and acid dyes on chrome tanned leather ranges from 4-6 which could be ascribed to the coupling components used.

The synthesized dyes 1a and 2a values of light fastness can be attributed to the introduction of the thiophene ring ortho to the azo group resulting in a significant improvement in light fastness as compared to dyes 3a and 4a which is in consonant with the work of Patel *et al.,* (2003). Most of the dyes gave a good to very good light fastness. This may be attributed to the molecular structure of the dyes, planarity and dye substituents that provided shield from radiant energy on azo chromophores, and which conferred good light fastness properties on the dyed substrates (Sakoma *et al.,* 2012).

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

6.1 Summary

Monoazo dyes of lower molecular weight derived from 2-aminothiophenes and conventional amines with dye exhaustion values ranging from 60 % to 78 % on polyester fabric and 80 % to 87 % on chrome tanned leather were successfully synthesised. The molar mass of the synthesized intermediates ranges from 257-285 g/mol while that of the synthesized dyes ranges from 305-614 g/mol. The synthesised intermediates and dyes exhibited fairly well-defined melting points characteristics of pure compounds. The infrared spectra of the synthesised intermediates showed absorption peaks in the range 2199.1-2206.6 cm^{-1} due to the presence of the cyano group, NH stretching vibrations for the two intermediates appeared in the range 3198-3421.7 cm^{-1} while the carbonyl absorption bands were observed in the range 1602-1695 cm^{-1}. As seen from the IR spectra of the synthesized dyes, they all gave absorption peaks due to azo group -N=N- stretching vibration at the range 1416.4-1599.0 cm^{-1}, the C-H stretching vibration band at 2993.1-2788.0 cm^{-1}; an absorption peak in the region 2281.1-2214.0 cm^{-1} due to V_{CN} was observed for the synthesized azo dyes 1a, 1b, 1c, 2a, 2b, 2c, 3c and 4c, while NH stretching vibration was observed at the frequency range of 3552.2-3302.4 cm^{-1} for synthesized azo dyes 1a, 1b, 1c, 2a, 2b, 2c, 3a, 3b, and 3c. The IR spectra of some of the synthesized azo dyes also showed an absorption peak in the region of 1722.0-1602.8 cm^{-1}, attributed to C=O stretching vibration for azo dyes 1a, 1b, 1c, 2a, 2b, 2c, 3c and 4c, respectively. An absorption peak in the region 3399.3-3309.9 cm^{-1} due to OH stretching vibration was observed for azo dyes 4a, 4b and 4c, while the observed peak in the region 1271.0-1114.5 cm^{-1} attributed to C-N bending vibration was seen in the synthesized azo dyes 4a and 4b, respectively.

The mass spectra of the intermediates 1 and 2 are fully consistent with the assigned structures: in most cases, intense molecular ion peaks were observed. Thus intermediates 1 and 2 showed intense molecular ion peaks at m/z 259±2 and 282±3, consistent with the molecular formulae $C_{13}H_{11}N_3OS$ and $C_{15}H_{15}N_3OS$ respectively while that of the synthesised dyes 3a, 4a and 4b showed molecular ion peaks at m/z 308±3, 366.4±5 and 394.0± respectively which is consistent with the molecular formula of the dyes. Thus, the slight difference in numerical value of the molecular weight of the dyes can be attributed to certain elements with high isotopic abundance (Khoptar, 2008).

The UV-visible spectra analysis of the compounds showed absorption in the visible region greater than 400 nm which were characteristic of all compounds of the dyes studied but that of the synthesised heterocyclic disperse dyes 1a-2c were more bathochromic than dyes 2a-4c which is due to the introduction of the cyano group as an electron–withdrawing substituent onto the thiophene ring and also the replacement of the five membered ring sulphur heterocyclic diazo component with the six-membered analogues as the diazo component of their respective azo dyes (Griffiths, 1984; Egli, 1991; Towns, 1999).

The fastness properties of the synthesised dyes applied on polyester fabric and chrome tanned leather showed good, very good and excellent results. For wash fastness, it was between 5 (excellent) and 3 (good), for light fastness it was between 6 (good) and 4 (moderate). The remarkable degree of levelness and brightness after washing indicate good penetration and excellent affinity of the dyes to the fibres (Convington, *et al.*, 2005).

The antimicrobial activities of the synthesized dyes were studied against six different microbes using the Agar Well Diffusion method and the zone of inhibition ranges from 03-34 mm except for dye 3b which has no effect on *Candida albicans, Candida krusei* and dye 4b which has no activity on *Pseudomonas aeruginosa*. As low MIC value of 12.5 mg/ml and MBC/MFC value of 12.5 mg/ml of some of the synthesized dyes had activity against *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Candida krusei* and *Candida albicans*;

this shows that most of the dyes are not only bacteriostatic/fungistatic but are also Bactericidal/fungicidal in their mode of action against the microorganisms. All synthesized dyes with heterocyclic system containing thiophene ring possessed enhanced antimicrobial activity. This strong antimicrobial activity may be due to attachment of the thiophene moieties which is in agreement with the work of Shridhar *et al.,* (2011).

6.2 **Conclusion**

A series of heterocyclic disperse and acid dyes based on 2-aminothiophene and conventional amines have been synthesized, their colouristic properties examined by application on polyester and leather substrates and their antimicrobial properties were assessed using the Agar Well diffusion method. These dyes gave mostly brown, deep purple, yellow and orange shades on the dyed polyester and leather depending on the coupling components and with generally good fastness properties. Exhaustion of some of these dyes on polyester and leather substrates were very good and indicate that the dyes have good affinity and solubility in the dyed substrates. The dyeings show very good to excellent fastness to washing and moderate to good light fastness properties. The remarkable degrees of levelness after washing indicate good penetration and affinity of these dyes for the dyed polyester fabric. The synthesized dyes show remarkable biological activities against some of the pathogenic microorganisms and therefore can be used in the manufacture of fabric for white coat and laboratory coat worn by Medical Doctors and Laboratarians, respectively.

6.3 Recommendations

a) Toxicological and pharmacological screening should be carried out on the synthesized dyes.

b) Further structural elucidation of the synthesized dyes using NMR and high resolution Mass Spectrometry should be conducted.

c) Possible Investigation of the antimicrobial properties of the dyed substrates.

d) Further investigation of the antimicrobial properties of the synthesized dyes against other drug resistant pathogenic microorganisms should be carried out.

CONTRIBUTION TO KNOWLEDGE

The study established that:

1. New heterocyclic disperse dyes with o-Acetoacetanilide and N-(2, 4-dimethylphenyl)-3-oxobutyramide to form 2-aminothiophene intermediates and coupled with N,N-dimethylaniline, N,N-diethylaniline and Dodecyl pyridone have been synthesized.
2. The dyes were successfully applied on polyester fabric and chrome tanned leather with good colouristic properties.
3. The antimicrobial properties of the synthesized dyes were successfully evaluated and were found to possess biological activities against some selected pathogenic microorganisms.

REFERENCES

Abrahart, E.N. (1977), *Dyes and their Intermediates,* 2nd Edition, Published by Edward Arnold Publishers, London. pp 1-9, 72.

Aftalion, F. A. (1991). *History of the International Chemical Industry*. Philadelphia: University of Pennsylvania Press, pp. 256.

Alaa, S.A. and Tarek H.A (2006). Novel azo disperse dyes derived from aminothiophenes: synthesis and UV-visible studies. *Dyes and Pigments 7:* pp 8-17.

Allen R.L.M (1971). Colour Chemistry, London: Thomas Nelson and Sons Ltd. pp. 11–13.

Aspland, J. R. (1992). A Series on Dyeing: Disperse Dyes and Their Application to Polyester. *Textile Chemical Colouration*, 24(12): 18–23.

Avci GA, Ozkinali S, Ozluk A, Avci E, Kocaokutgen H. (2012); Antimicrobial activities, absorption characteristics and tautomeric structures of o,o'-hydroxyazo dyes containing an acryloyloxy group and their chromium complexes. *Hacettepe Journal Biology. Chem.* 40(2):119-26.

Az.EL-Sonbati, A.A.M. Belal, S.I. EL-Wakeel, and M.A. Hussien, (2004); *Journal of. Spectrochemistry ACTA A,* (60), 965-970.

Beer, J. J.(1959). *The Emergence of the German Dye Industry*. Urbana, Illinois: Univeristy of Illinois Press, pp.345.

Bird, C.L and Boston W.S (1975) Eds. *The Theory of Colouration of Textiles.* Dyers Company PublicationTrust (Bradford, UK) pp 25-35

Brent, S (1987) Trouble Shooting in Dyeing. *American Dyestuff Reporter.* March-April issue, pp 10-15

Catinosc, R.E. (1985); Azo dyes In: Grayson M., editor, concise encyclopedia of chemical technology. New York, 142-144.

Chatterjee, P.K (1988) Absorbency in: *Textile Science and Technology, Vol 7, 2nd* Edn. (Amsterdam, Holland: Elsevier) pp 1-56

Christie, R.M. (2001); Colour Chemistry, the Royal Society of Chemistry, RSC Paperbacks, pp. 1–11.

Convington, A.D.; Evans, C.S.; Lilley, T.H. and Suparno, (2005); Collagen and Polyphenols: New Relationships and New Outcomes. Part 2. Phenolic Reactions for Simultaneous Tanning and Colouring. 100: 336-343.

Cunningham A.D (1996). Identifying Critical Machinery and Dye parameters for Successful Rapid Dyeing of Polyester. *Journal of Textile Chemist and Colorist* 28: 23

David, G.D and Roy S.S (1989): Laboratory Course in Dyeing. Dyers' Company Publication Trust, Bradford, pp 102-104

Ebenso, E.E.; Alemu, H.; Umoren, S.A. and Obot, I.B., (2008); Inhibition of mild steel corrosion in Sulphuric Acid using Alizarin yellow G.G. Dye and Synergistic Iodide Additive. *International Journal of Electrochemistry and Science.* (3):1325-1339.

Egli, R (1991). The chemistry of blue disperse dyes, past and present. In: Peters A.T, Freeman H.S, editors. Colour Chemistry; The design and synthesis of organic dyes and pigmrnts. London: Elsevier Science Publishers Ltd, pp 132-140

El-Kashouti, M. A., El- Molla, M. M., El-Sayad, H. S., Ahmad, K. A., Helal, M. H. and El-Gemeie, G. H. (2008). Synthesis of Several new Pyridine-2(1H) Thiones containing an Arylazo Function. *Pigment and Resin Technology*, 37(2): 80–86.

Emeruwa, A.I (2012). Antibacterial Substance from *Carica papaya* Fruit Extracts. *Journal of Natural Products*, 45 (2): 123 – 127.

Gerald, B. (1988). *The Manufacture Organic Colorants and Intermediate*. Bradford, England: Society of Dyers and Colourists, pp. 122- 134.

Giles, C. H. (Ed). (1974). *A Laboratory Course in Dyeing*. Bradford: The Society of Dyers and Colourists, pp 2-7.

Gopalakrishnan S., Nevaditha N.T. and Mythili C.V. (2011); Antibacterial activity of azo compounds synthesized from the natural renewable source, cardanol. *Journal of Chemical and Pharmaceutical Research 3(4)*:490-97

Gohl, E.P.G and Vilensky, L.D (1980): *Textile Science*, Melbourne, Australia: Longman pp 25-48

.

Gregory, P.D., Waring, R. and Hallas, G. (1990): *The Chemistry and Application of Dyes*, Plenum Press London. pp. 18 – 20.

Griffiths, J (1981): Recent developments in the colour and constitution of organic dyes. Review of progress in colouration and Related Topics, (11**):**37-50.

Griffiths, J (1982): Practical aspects of colour prediction of organic dye molecules. *Dyes and Pigments* (3):211-233.

Griffiths, J. (1984). Development in the Light Absorption Properties of Dyes, Critical Report of Applied Chemistry, Vol. 7, Black Well Scientific Publication, London. pp. 1-27.

Gordon, P.F. and Gregory, P. (1983); Organic Chemistry in Colour, Springer-Verlag, New York, pp. 95, 108-111.

Hallas, G and Town A.D (1996a). A comparison of the properties of some 2-aminothiophene derived disperse dyes. *Dyes and Pigments 31* (4) 273-289.

Hallas, G and Town A.D.(1996b). Dyes Derived from Aminothiophene: Part 1; Synthesis of Some Heterocyclic Disperse Dyes Using Gewald Reaction. Dyes and Pigments 32(3) 135-149.

Hallas, G and Towns, A.D. (1997a). Dyes derived from Aminothiophenes. Part 3: Applications of some disperse dyes derived from 2-aminothiophenes to hydrophobic fibres. *Dyes and Pigments* (33), 215–228.

Hallas, G and Towns, A.D. (1997b). Dyes derived from Aminothiophenes. Part 4: synthesis of some nitro-substituted thiophene-based azo disperse dyes. *Dyes and Pigments*. 33 (4) 319-336

Hari R. and Maradiya H. (2012); *Journal of Saudi Chemical Society*, (16):69–74.

Heywood. D. (2003); Textile Finishing, Society of Dyers and Colourists.

Himani N.C, Jyotsna S.M, Ramakanth P, and Arvind J.M. (2010). Synthesis, characterization and antibacterial activity of some novel azo-azoimine dyes of 6-bromo-2-naphthol. *International Journal of ChemTech Research CODEN(USA): IJCRGG ISSN : 0974-4290,* 2(3):1823-1830.

Ingamells, W. (1993). Colour for Textiles: A User's Handbook. Bradford, United Kingdom: Society of Dyers and Colourists, pp. 78-252.

Iyun, O. A, (2008), Synthesis of Dyes Derived From 2-Amino Heterocycles and Their Dyeing Performance on Polymeric Materials. M.Sc Thesis, Abubakar Tafawa Balewa University Bauchi. pp 88, 91-94.

Jack, Jie Li (2005). *Name reactions in heterocyclic chemistry*. Hoboken NJ. Wiley InterScience. pp180-285

Jae-Hong Choi, Jong-yun Choi, Hyun-young Lee, Andrew D. Towns, and Chun Yoon (2008): Novel azo dyes derived from phthalimide. Part 2: Dyeing properties and colour fastness on polyester fibres. *coloration Technology.* 124, pp 364-369

Joonseok, K. (2011). Dyeing with Disperse Dyes. In Hauser, P. (Ed.), *Textile Dyeing.* Europe: In-Tech. pp. 195-220

Karci, F. and Ertan, N. (2005); *Coloration Technology*. 121(3), 153-157.

Karlm, K., Kevin M.S. and Roger, G. (2003). *The Porphyrin Handbook; Application of Phthalocyanines*. New York: Elsevier, pp.105.

Katritzky, A.R. and Rees, C.W. (1984). Comprehensive Heterocyclic Chemistry, Pergamon Press Oxford. Vol. 3, pp. 51.

Kent, J.A. (2007). *Handbook of Industrial Chemistry and Biotechnology*. USA: Jupiter, pp. 43-107.

Khalid A., Arshad M. and Crowley D.E. (2008); Accelerated decolorization of structurally different azo dyes by newly isolated bacterial strains. *Journal of Applied Microbiology and Biotechnology.* (78): 361-369.

Khoptar, S. M. (2008). Basic concept of analytical chemistry. New age international publisher, India pp 122-120, 183, 290-292, 450-457.

Kirkan, B. and Gup, R. (2008); Synthesis of New Azo Dyes and Copper (II) Complexes Derived from Barbituric Acid and 4-Aminobenzoylhydrazone. *Turkish Journal of Chemitry,* 32: 9-17.

Kusic, H., Juretic, D., Korivanac, V., Marin, V. and Bozic, A. L. (2011); *Journal of Hazardous,* 185: 1558-1568.

Kyriaki, L. and Eforia G. (2002): Heterylazo disperse dyes derived from substituted N,N-bis-β-hydroxy- and N,N-bis-β-acetoxy-ethylaniline. *Dyes and Pigments* 53: 73-78.

Li, Y.; Shan, Z.H; Shao, S.X and Shi, K.Q. (2006); *Journal of Society Leather Technologists and Chemists. 5*: 214-216.

Lan. Y. J.; Shi, B. and Li. S. (2000); Types and Functions of Dyeing Assistant for Leather, Chinese Leather, China. 29(23):12-15.

Ma, M. and Sun, G. (2005); *Antimicrobial cationic dyes. Part 3: simultaneous dyeing and antimicrobial finishing of acrylic fabrics. Dyes and pigments,* 66(1): 33-41.

Maradiya H.R. (2001): Synthesis of azobenzo[b]thiophene derivatives and their dyeing performance on polyester fibre. *Turkish Journal of Chemistry 25*: 441-445

Maradiya, H.R and Patel V.S. (2002a): Synthesis of Novel Azo Containing the Thiophene Moiety. *Chemistry of Heterocyclic Compounds* 38(11): 1324-1330.

Maradiya, H.R and Patel V.S. (2002b): Thiophene based monoazo disperse dyes for polyester fabric. *Journal of the Serbian Chemical Society,* 67(1): 17-25

Maradiya H.R (2010): Synthesis and Dyeing performance of some novel thiazoe azo disperse dyes. *Journal of the Saudi Chemical Society,* 14: 77-81

Marini, A. and Munoz L. (2010); *What is solvachromism. Journal of Physical Chemistry B.* 27(4): 114-365

Mann (1969); A Handbook on Nigerian Hides and Skins, Printed by Government Printer, Kaduna.

Mclaren, K. (1983). *The Colour Science of Dyes and Pigments*. Illinois: Adam Hilger Ltd., pp. 186.

Mohammad K.Z, Mokhtari J. and Nouri M. (2010): Color Technology, 126:81

Muralidharan, D and Sandra Rao (2005): *Journal of the Society of Leather Technologist and Chemists,* (75):179.

Nejati, K., Rezvani, Z. and Massoumi, B. (2007); *Dyes and Pigments, 75*, pp 653

Nkeonye P. O. (1987). Fundamental Principles of Textile Dyeing, Printing and Finishing, Ahmadu Bello University Press Ltd, Zaria. pp 34-35.

Nunn, D.M. (1979). The dyeing of synthetic polymer and acetate fibres. Dyers Company Publication Trust, Bradford, pp 243-256

Otutu, J.O., Osabohien, E, and Efurhuvwe, E.M. (2011); Synthesis and spectral properties of hetaryl monoazo dyes derived from 2-Amino-5–nitrothiazole *Oriental Journal of Chemistry*, 27(4): 1389-1396.

Ozan, A. (2011).Maximizing the Washing Fastness of Dyed Poly(Lactic) Acid by Adjusting the Amount of Air During Convectional Reducing Clearing. *Textile Research Journal, 81(10)*: 1049-1074.

Page C.T., Gabagnou, C and Tidei, A. (1997); Leather International, 199(4664): 37-40.

Patel P.S, Patel S.K, Patel K.C. (2003); Synthesis of Heteroaryazo Disperse Dyes and Their Dyeing Performance on Various Fibres. *Arch. Applied Science Research.* 81: 321

Patel P.S. (2012); Studies on synthesis and dyeing performance of disperse azo dyes based on Schiff base of ninhydrin and 3-amino phenol. *Arch. Applied Science Research*, 4(2):846-51.

Peter, J.M. and Anthony, S. T. (1992). A History of the International Dyestuff Industry. *American Dyestuff Reporter*, Volume 81. Retrieved April 21, 2016 from: http://www.colorantshistory.org/HistoryInternationalDyeIndustry.html

Peter, A.T. and Gbadamosi N.M.A (1992): 5,6-(6,7)-Dichlorobenzothiazolylazo dyes for synthetic polymer fibres. *Dyes and Pigments (18)* 115-123

Ramasami, T. (2001): *Journal of American Leather Chemist Association*, 96, 290-304.

Robert, T.M., Robert, N.B. and Bhattacharjee, S.K. (2011). Organic Chemistry. 6th edition. New Delhi. Pearson Prentice Hall, pp. 1096 – 1097

Sabnis, R.W; Rangnekar, D.W. and Sonawane N.D. (1999). 2-Aminothiophene by the gewald reaction. *Journal of Heterocyclic Chemistry*, 36: 333-345

Sabnis, R.W; Rangnekar, D.W (1999). *Indian Journal of Fibre Textile Research.* (17) 58

Sakoma, K.J., Bello, K.A. and Yakubu, M.K. (2012). Synthesis of some azo disperse dyes from 1-substituted 2-hydroxy-6-pyridon derivatives and their colour assessment on polyester fabric. *Open Journal of Applied Science*, 2(1): 54-59.

Sarkar, K (1980). Theory and Practice of Leather Manufacture, Revised Edition, Ajoy Sorcar, pp 69-232.

Samieh, F., Ahmad, M.T., Hooshang, H. and Hojatollah, K. (2008); A synthesis of some new 4-arylidene-5(4H)-oxoazoloneazo dyes and an evaluation of their solvatochromic behaviour. *ARKIVOC*, XIV 115-123.

Shore J. (1990). Colorants and Auxillaries. Vol 1, Bradford SDC, Pp 9–24

Simu G.M., Dragomirescu A., Grad M.E., Savoiubalint G., Andoni M. and Bals G. (2010); Azo compounds with antimicrobial activity. 14th Int. Electron. Conf. Syn. Org. Chem. ECSOC-14, 1–30.

Shridhar, H., Keshavayya, J., Joy Hoskeri, H. and Shoukat Ali, R. A. (2011); Synthesis of Some Novel Bis 1,3,4-Oxadiazole Fused Azo Dye Derivatives as Potent Antimicrobial Agents. *International Research Journal of Pure & Applied Chemistry 1(3): 119-129.*

Srinivasan, D., Nathan, S., Suresh T. and Perumalsam, P.Z. (2001); Antimicrobial activities of certain Indian medicinal plants used in Folkloric medicine. *Journal of Ethnopharmacology,* 74 (3): 217 - 220.

Stork, G., Deqiang, N., Fujimoto, A., Koft, E. R., Balkovec, J. M., Tata, J. R., Dake, G. R. J.(2001). Synthetic Dyes and Development of Organic Chemistry. *American Chemical Society*: 123, 3239

Swati.G., Romila, K., Sharma, I.K. and Verma, P.S. (2011); Synthesis, Characterization and Antimicrobial Screening of Some Azo Compounds. *International Journal of Applied Biology and Pharmaceutical Technology,* 28 (9): 177-180

S.D.C (1991). Standard Methods for the Determination of the Colour Fastness of Textiles and Leather. 5th Edition. Bradford, pp 53-65

Thoraya A., Farghaly, Z. and Abdallah A. (2008); Synthesis, azo-hydrazone tautomerism and antitumor screening of N-(3-ethoxycarbonyl-4,5,6,7-tetrahydro-benzo[b]thien-2-yl)-2-arylhydrazono-3-oxobutanamide derivatives. *Arkivoc.* 17:295.

Thomas, C. G. (1979). Medical Microbiology, 4th edition. Texas, U.S.A. pp. 356-358

Towns, A.D. (1999); Developments in azo disperse dyes derived from heterocyclic diazo components, *Dyes and Pigments 42*, 3–28.

Traubel, H. and Eitel, K. (1977); Recent Developments in Leather Dyeing, Bayer Information for leather industry pp 67 – 77.

Trotman, E. R. (1970). Dyeing and Chemical Technology of Textile Fibres. England: Arnold, pp 453.

Tysoe, C. S (1994); Dyestuff Development, *Journal of Society of Leather Technologist and Chemist, Vol. 79, Pp 68.*

Venkataraman, K. (1978); The Chemistry of Synthetic Dyes, Vol, III, Academic press. , New York pp 40–44

Venkataraman K. (1972). The Chemistry of Synthetic Dyes, Vol. VI, Academic Press, London. Pp 287-291

Victor, M. Tormyshev, Dmitry V. Trukhin, Olga Yu. Rogozhnikova, Tatiana V. Mikhalina, Tatiana I. Troitskaya, and Anthony Flinn (2006). *SYNLETT No 16* pp 2559-2564

Wainwright, M. (2001). *Journal of Antimicrobial Chemistry*, 47: 1

Yadav, P.S., Devprakash, G. Senthikumar P. (2011): *Indian Journal of pharmaceutical Science and Drug Research*, 3(1): 1-7.

Yanapati, S., Sankarling, Paul and Rosan (1996): Sulfur Dyes-Constitution, Synthesis and Application Part (II). New York: Trade Publication, pp. 56.

Yusuf, Y. (2012). Synthesis and Application of Disperse Dyes derived from 2–Amino–4–Chloro–5–Formylthiazole onto Polyester and Nylon 6.6 Fabrics, pp 30-58. Unpublished Ph.D. Dissertation, Ahmadu Bello University, Zaria, Nigeria.

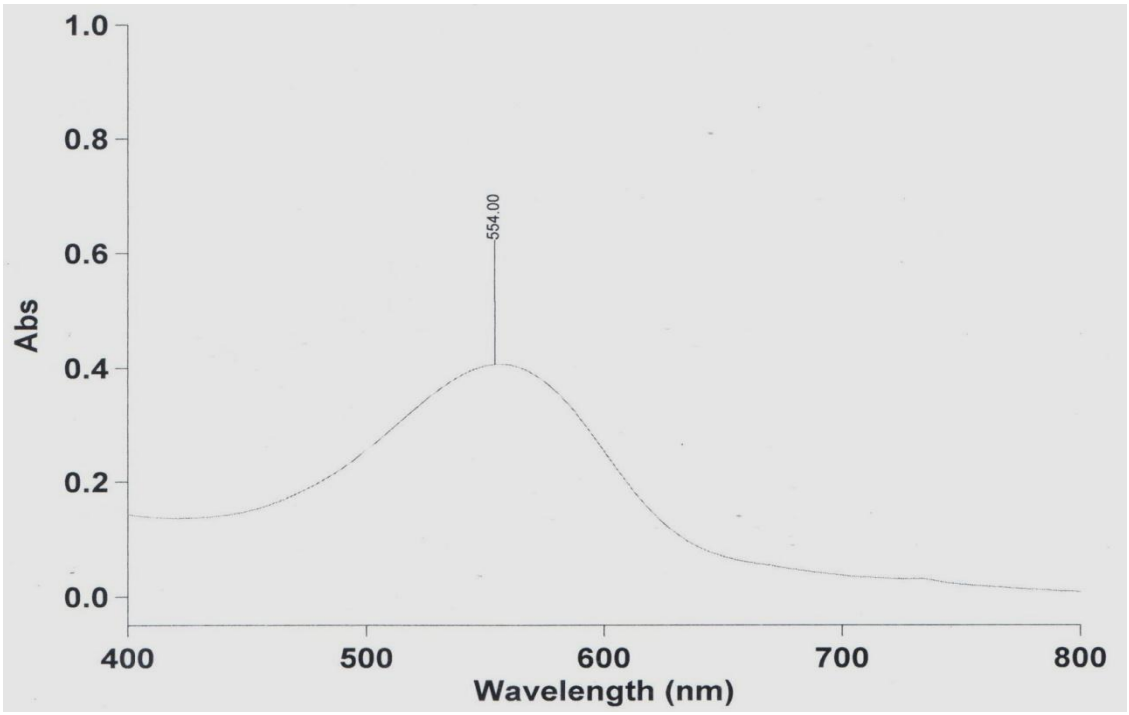
Yildiz, E and Boztepe, H (2002): Synthesis of Novel Acidic Mono Azo Dyes and an Investigation of Their Use in the Textile Industry. *Turkish Journal of Chemistry, 26*: 897-903

Yuh Wen Ho and Wei Hua Yao, (2006): Synthesis and properties of heterocyclic monoazo dyes derived from 3-cyano-4-trifluoromethyl-6-substituted-2-(1H)-pyridinethiones. *Dyes and Pigments*, 70: 60-69

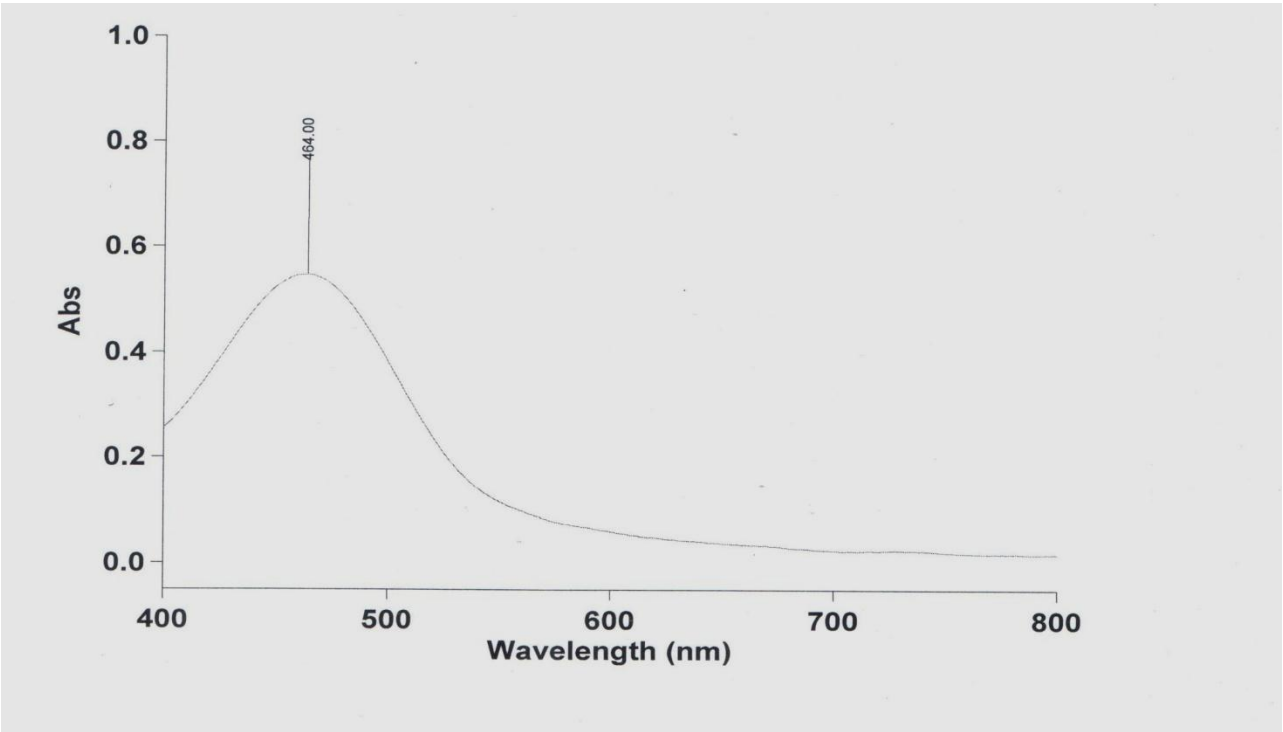
Zollinger, H. (2003). *Color Chemistry: Syntheses, Properties and Application of Organic Dyes and Pigments*. Germany:VCH, Weinheim, Pp 225-239.

APPENDIXES

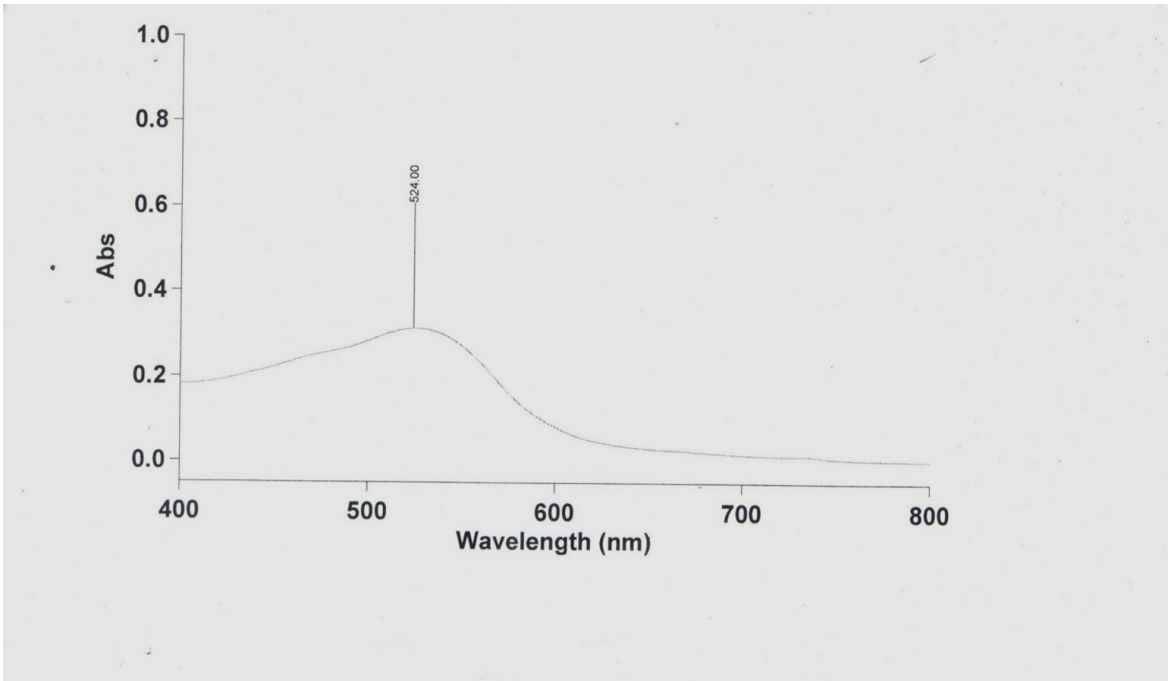
APPENDIX I: UV-VISIBLE SPECTROSCOPY OF DYES



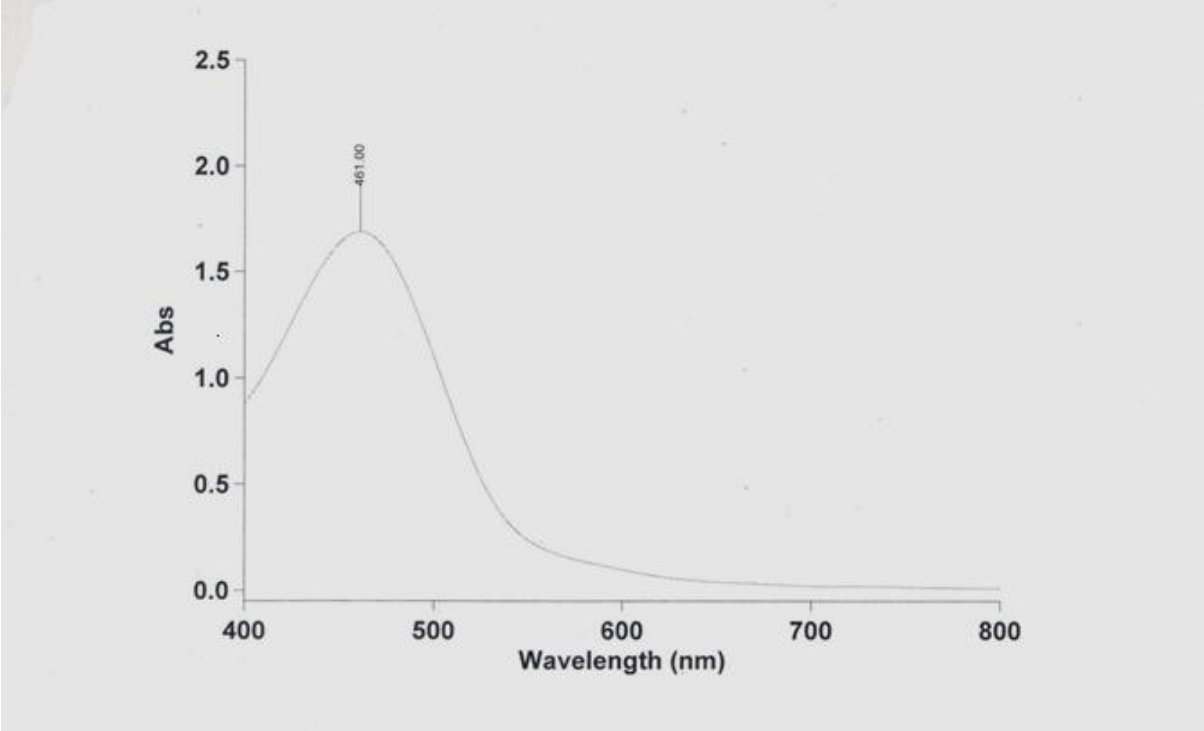
Uv-Visible Result of Dye 1a in DMSO



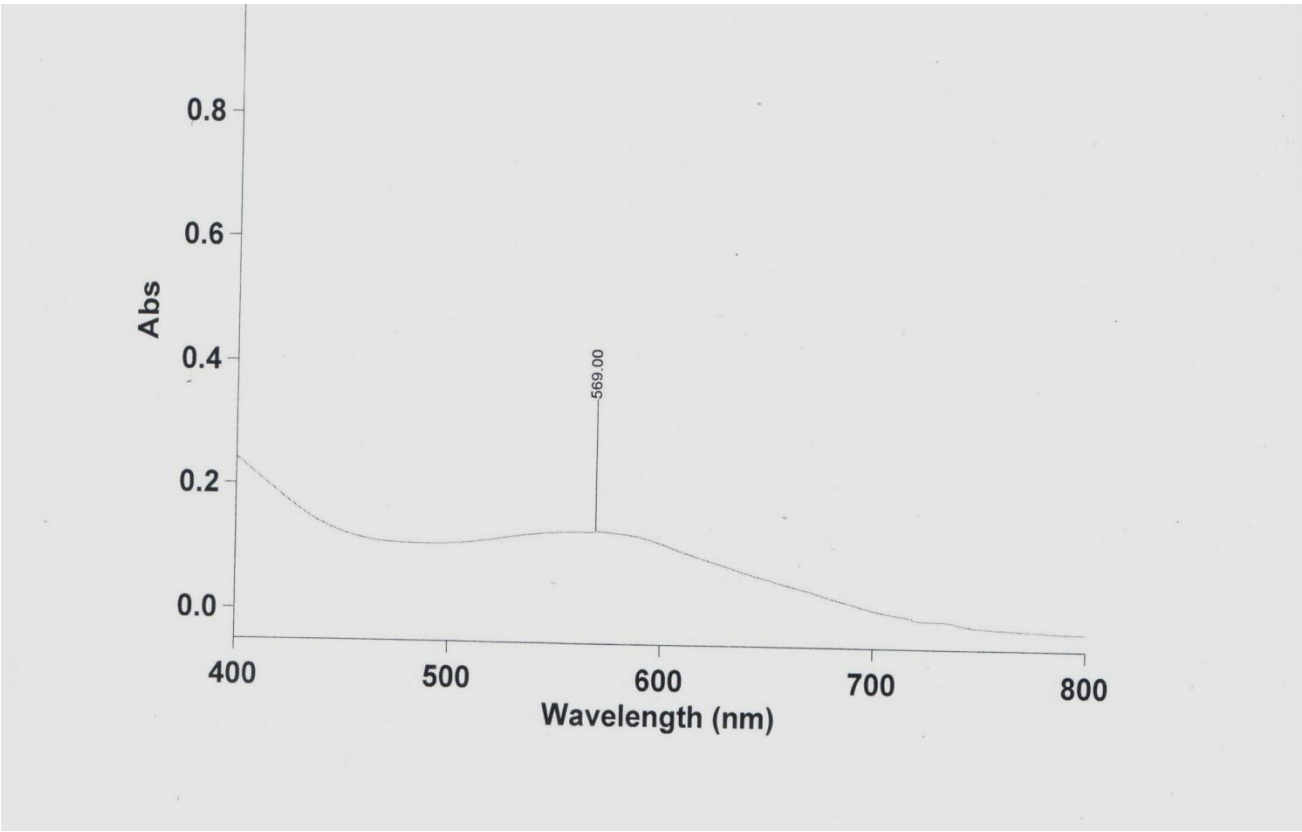
Uv-Visible Result of Dye 1a in Methanol



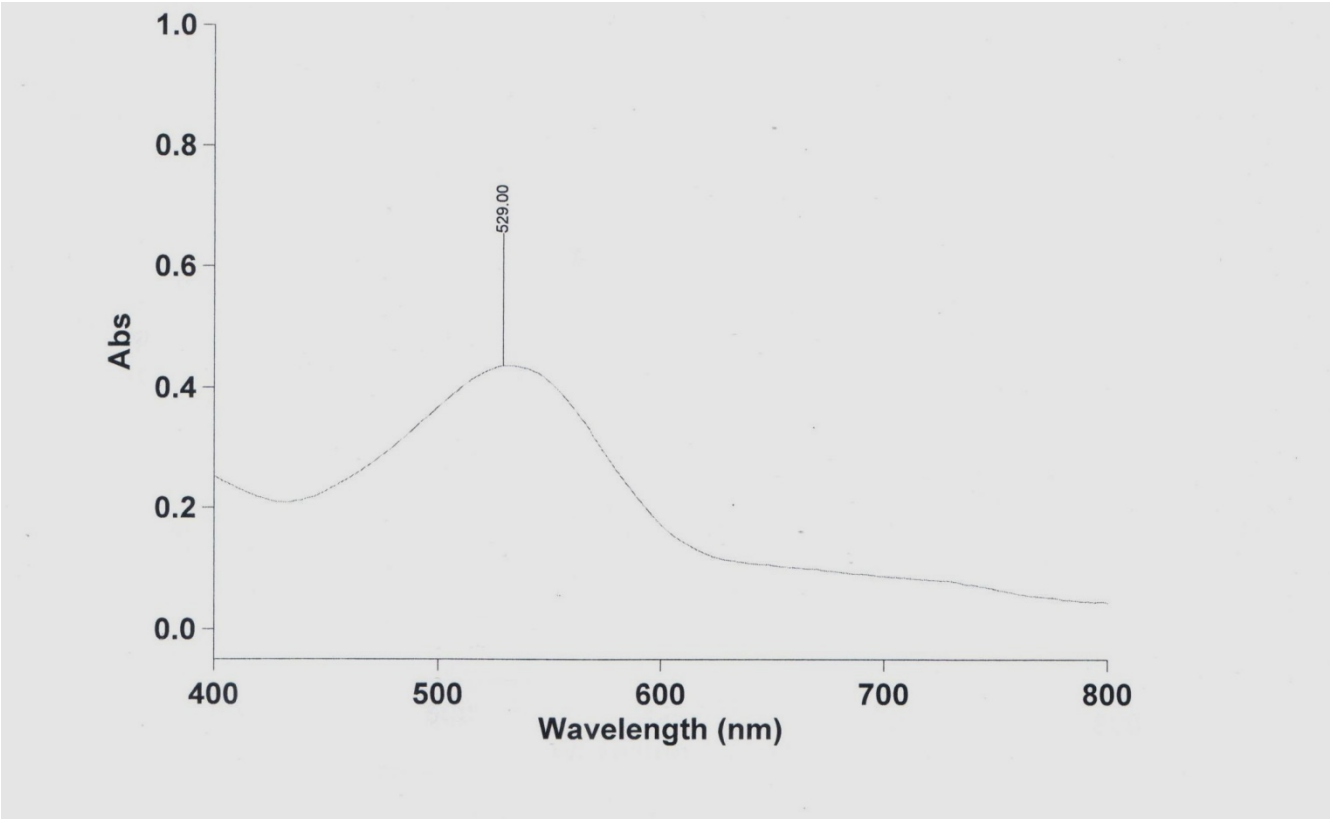
Uv-Visible Result of Dye 1b in DMSO



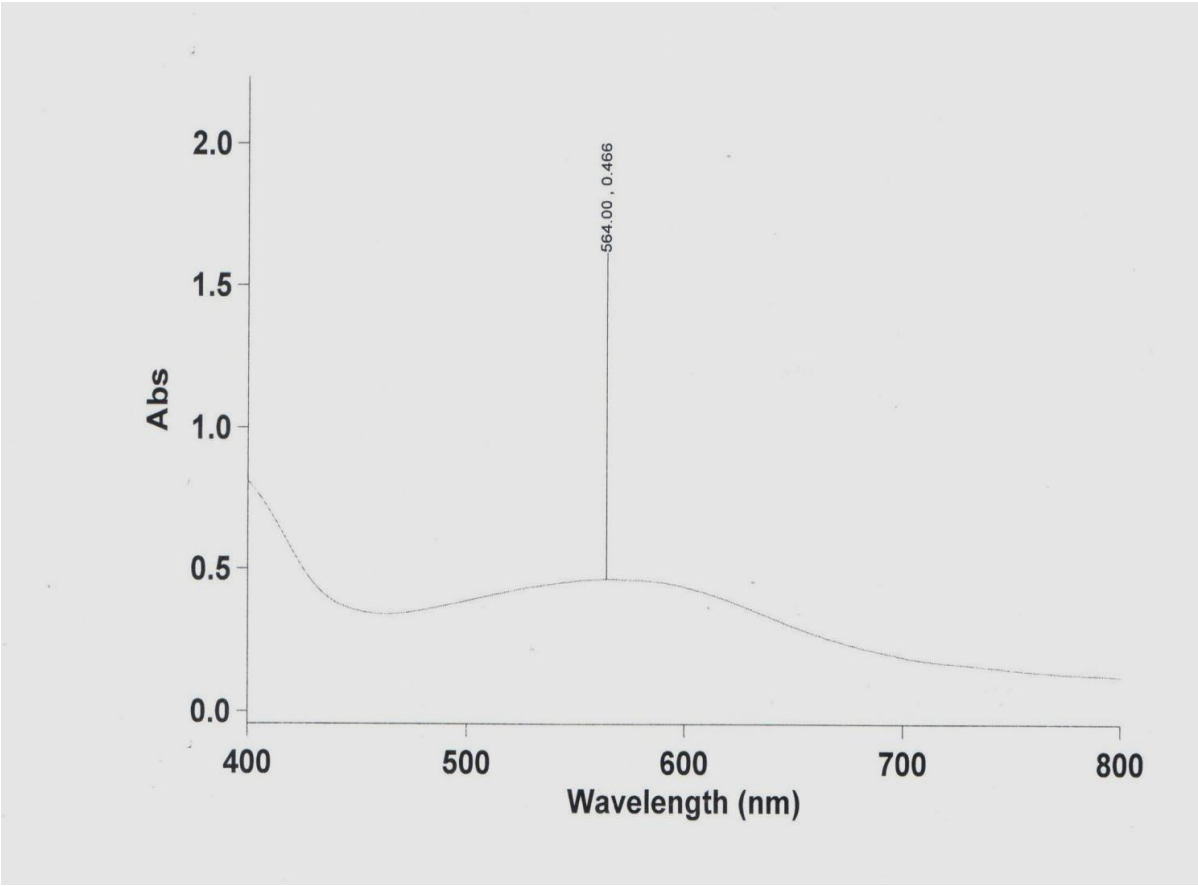
Uv-Visible Result of Dye 1b in Methanol



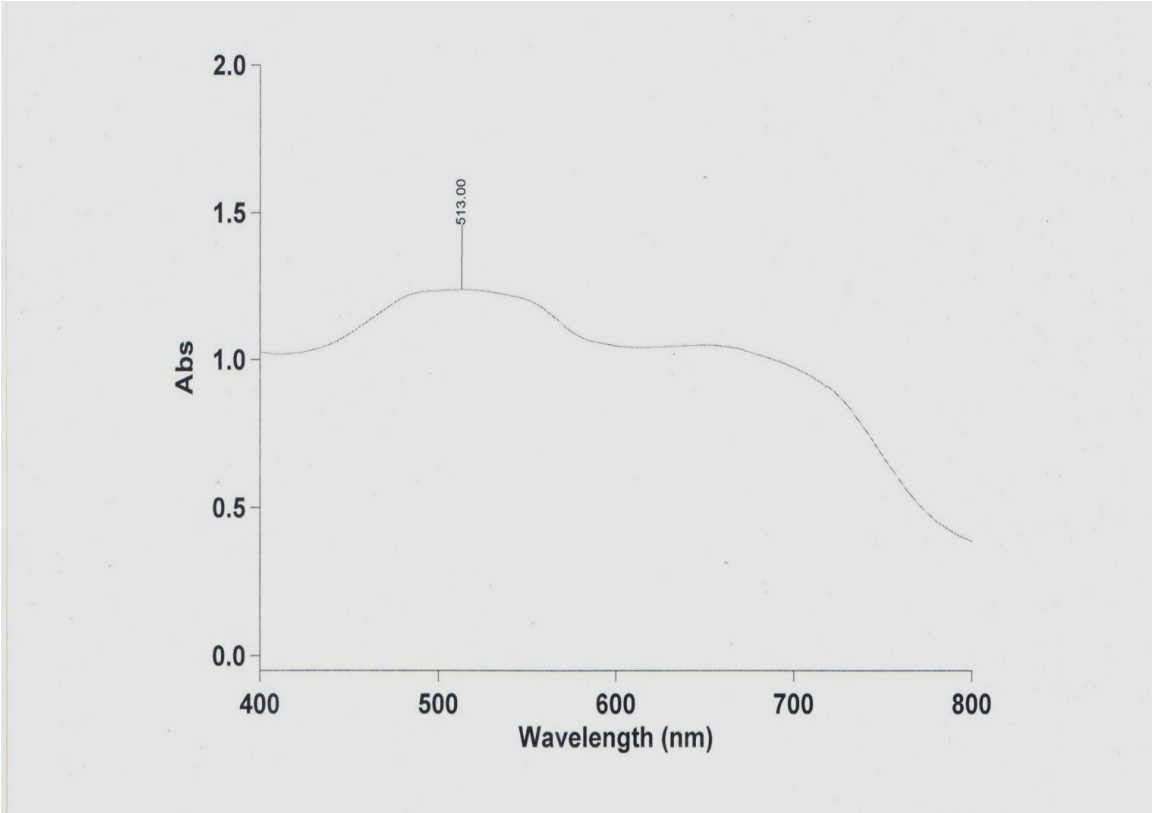
Uv-Visible Result of Dye 1c in DMSO



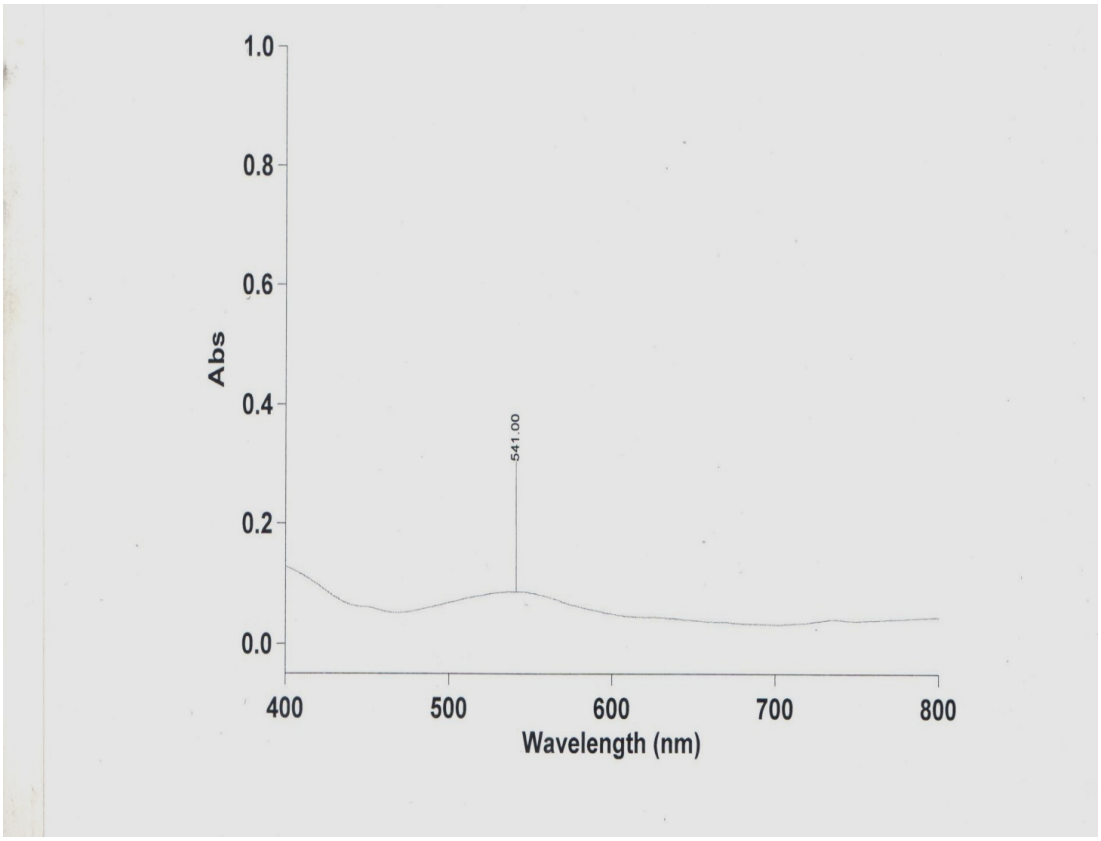
Uv-Visible Result of Dye 1c in Methanol



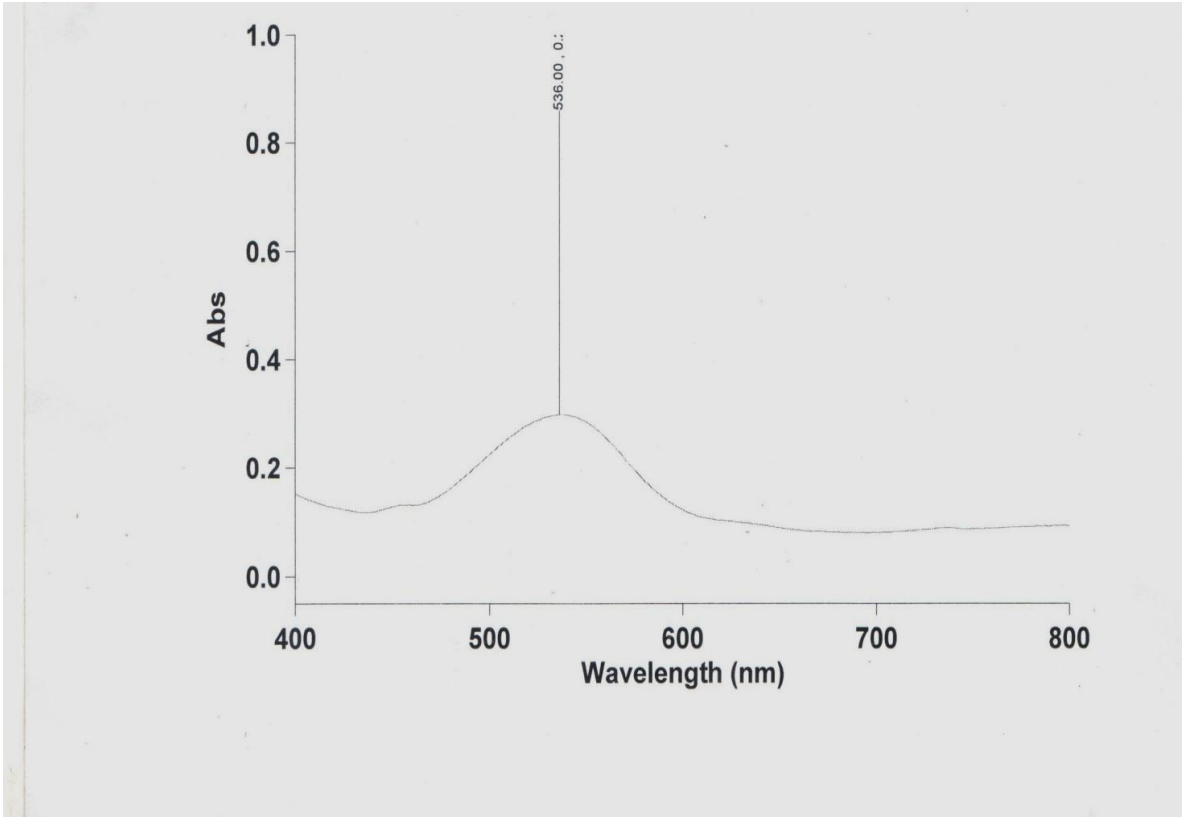
Uv-Visible Result of Dye 2a in DMSO



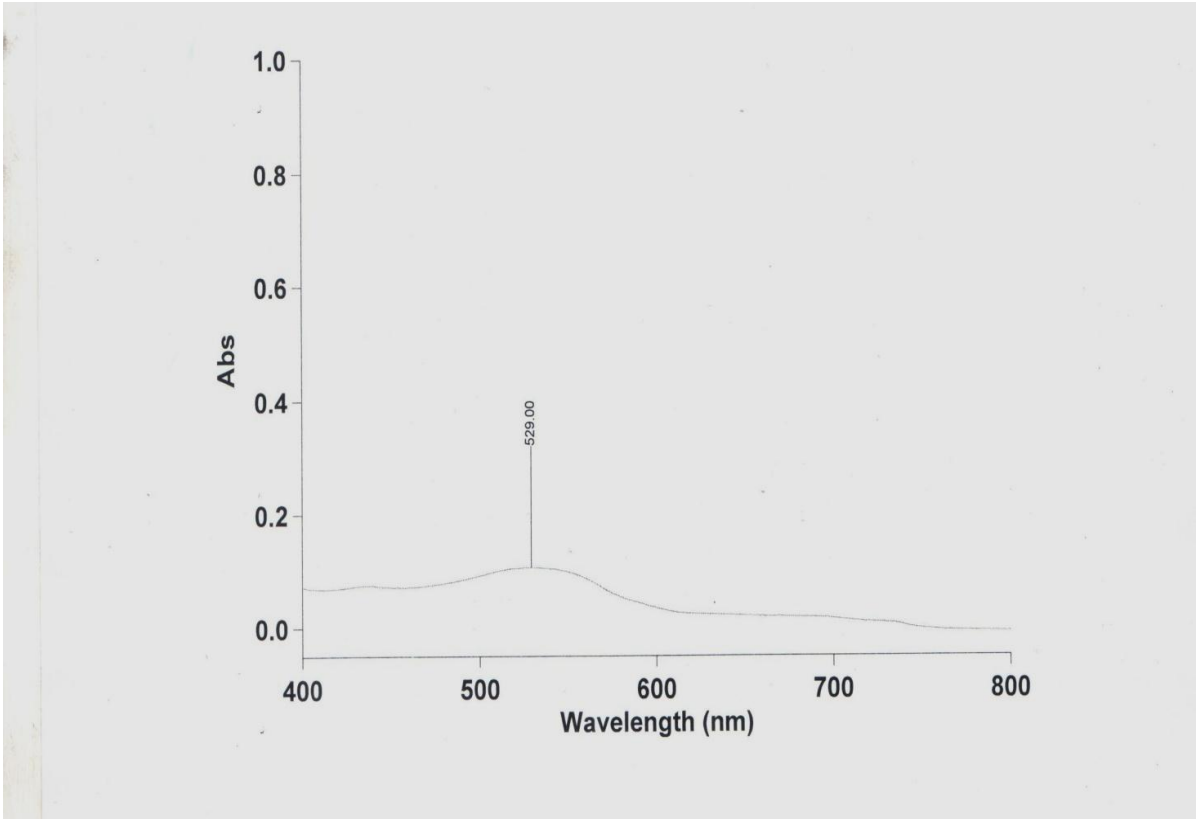
Uv-Visible Result of Dye 2a in Methanol



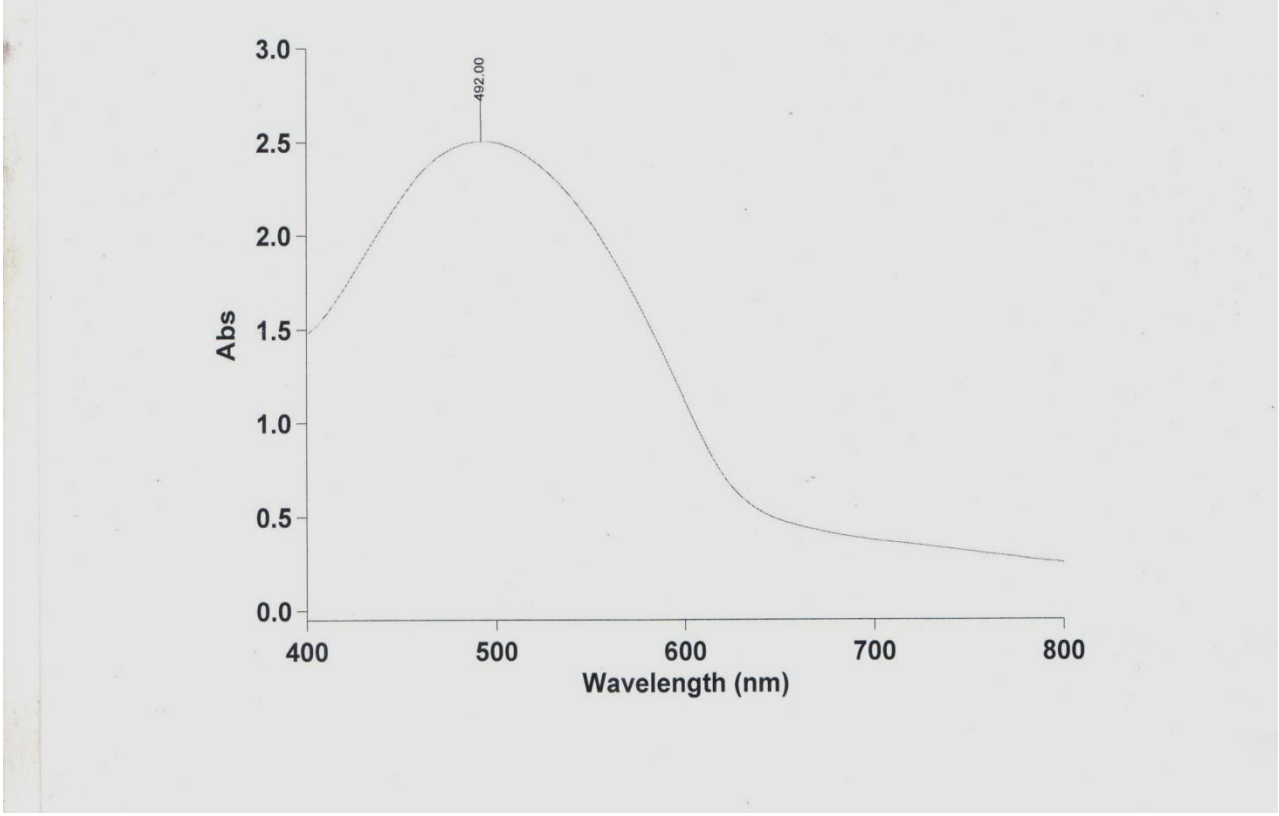
Uv-Visible Result of Dye 2b in DMSO



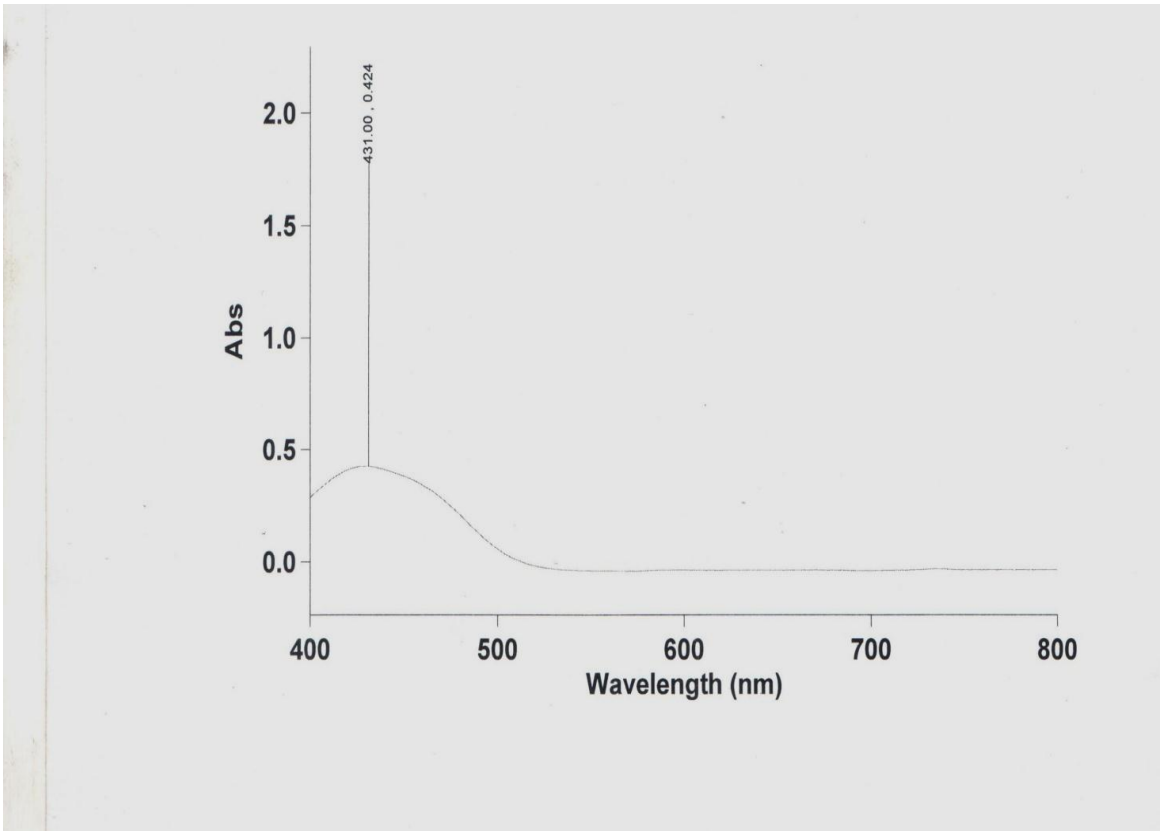
Uv-Visible Result of Dye 2b in Methanol



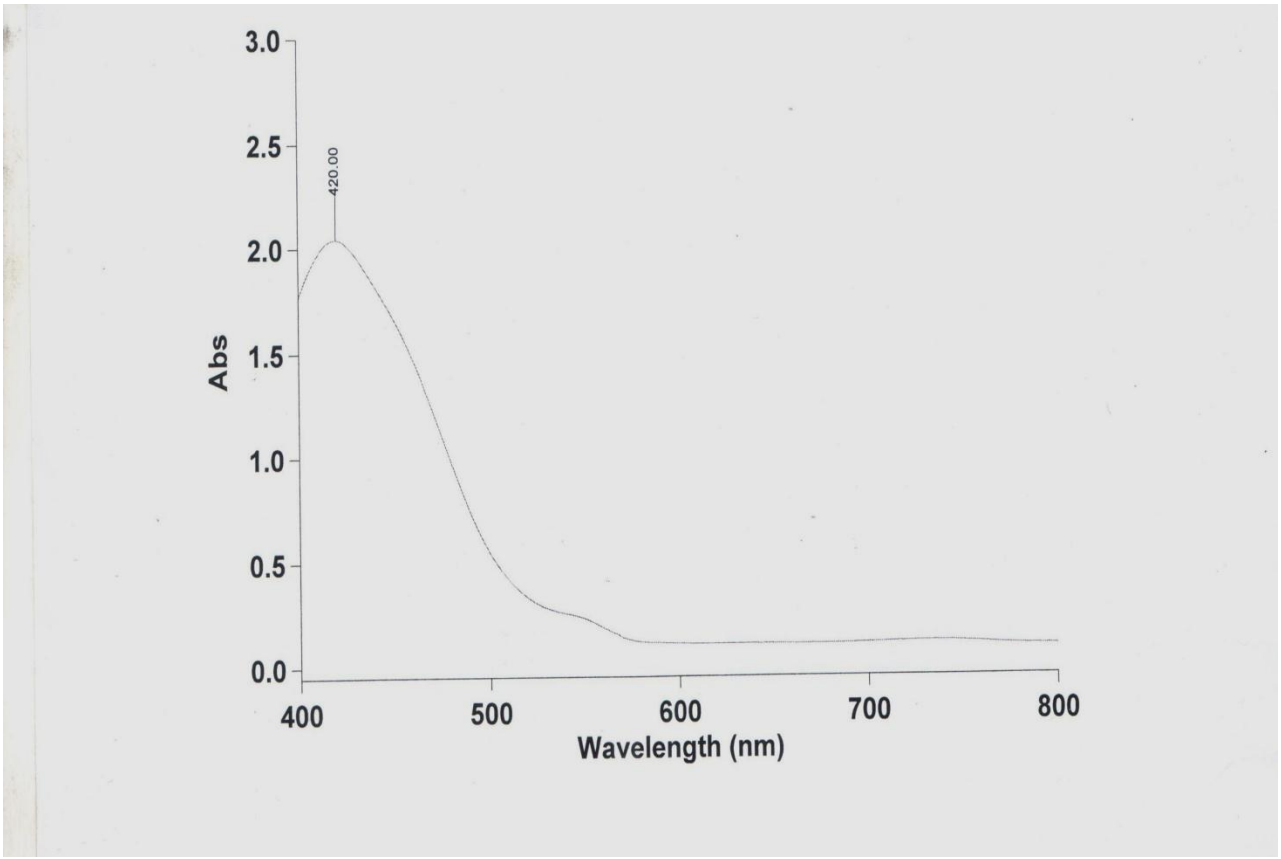
Uv-Visible Result of Dye 2c in DMSO



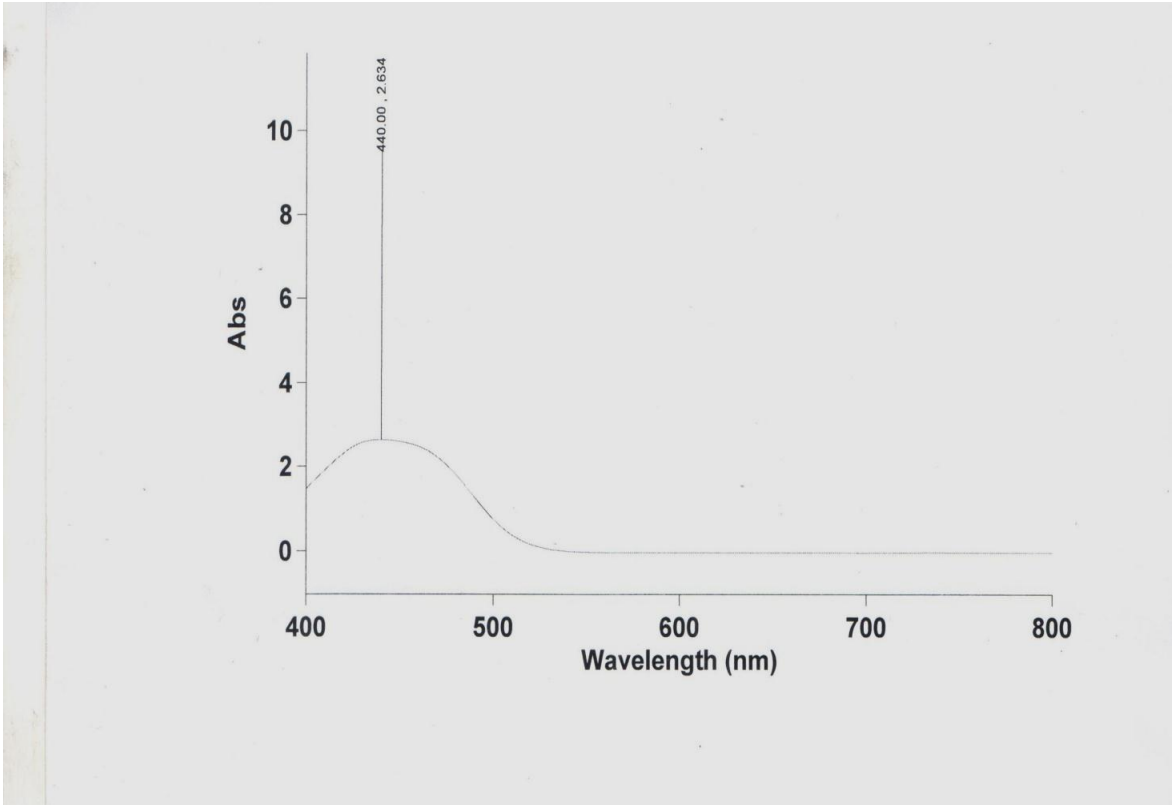
Uv-Visible Result of Dye 2c in Methanol



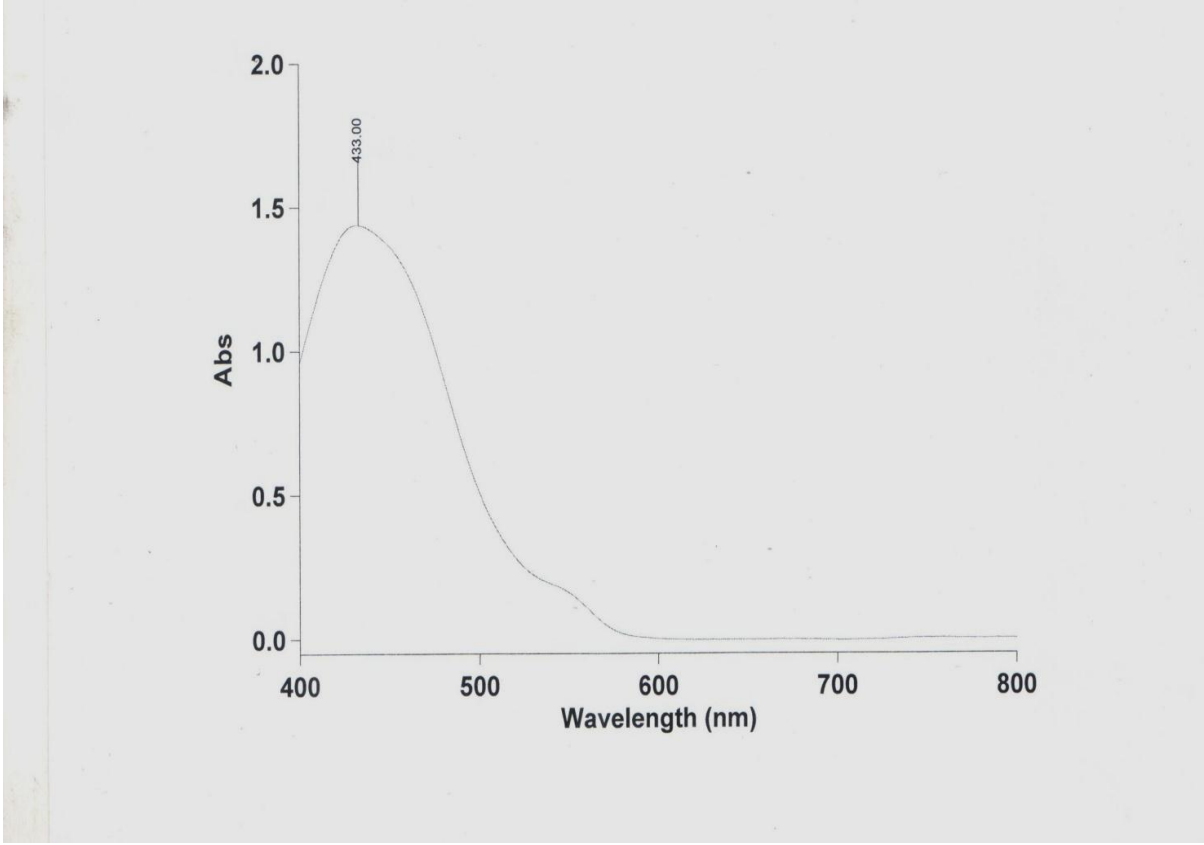
Uv-Visible Result of Dye 3a in DMSO



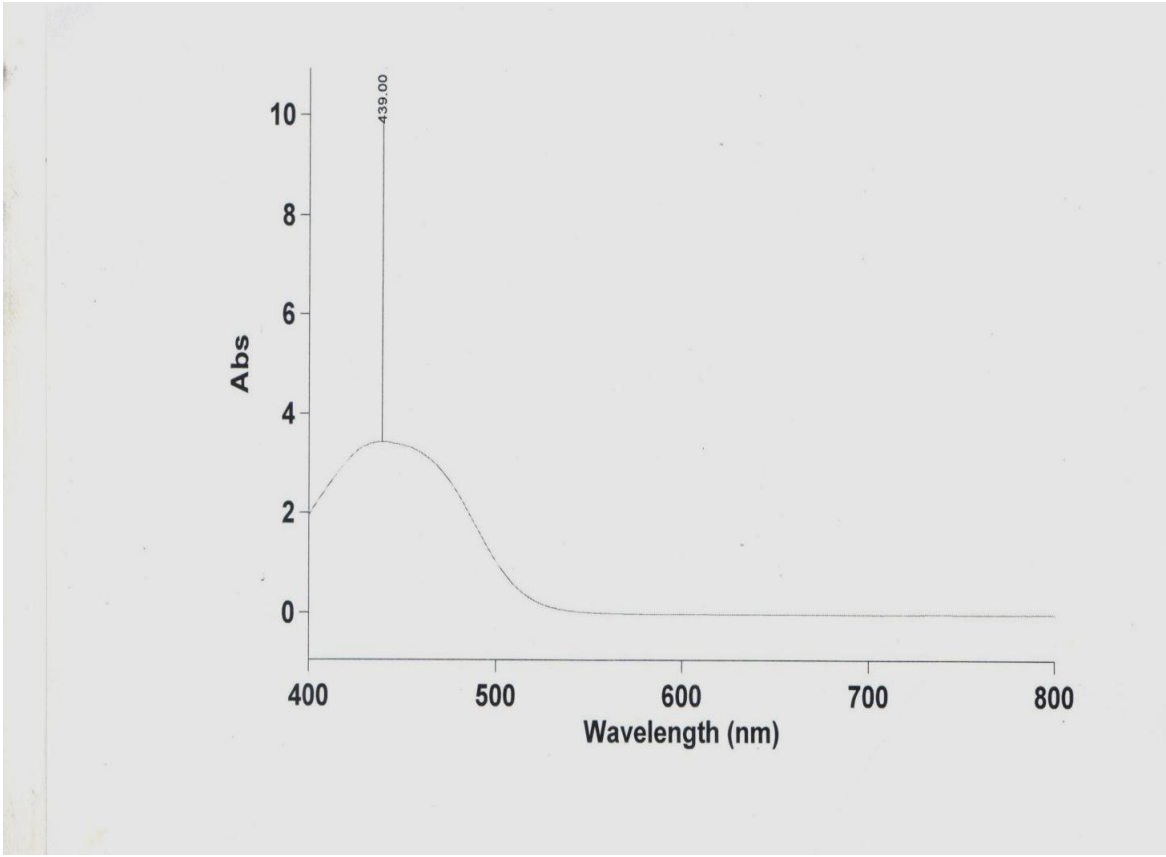
Uv-Visible Result of Dye 3a in Methanol



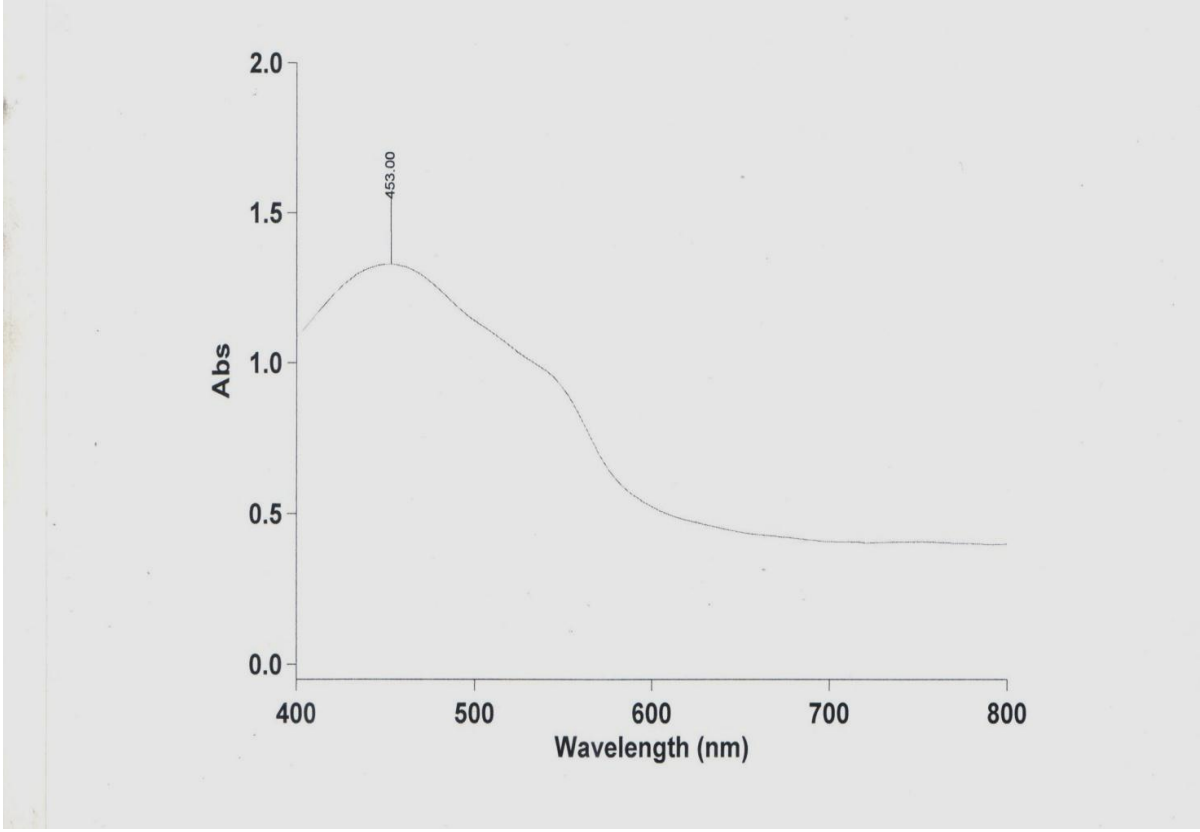
Uv-Visible Result of Dye 3b in DMSO



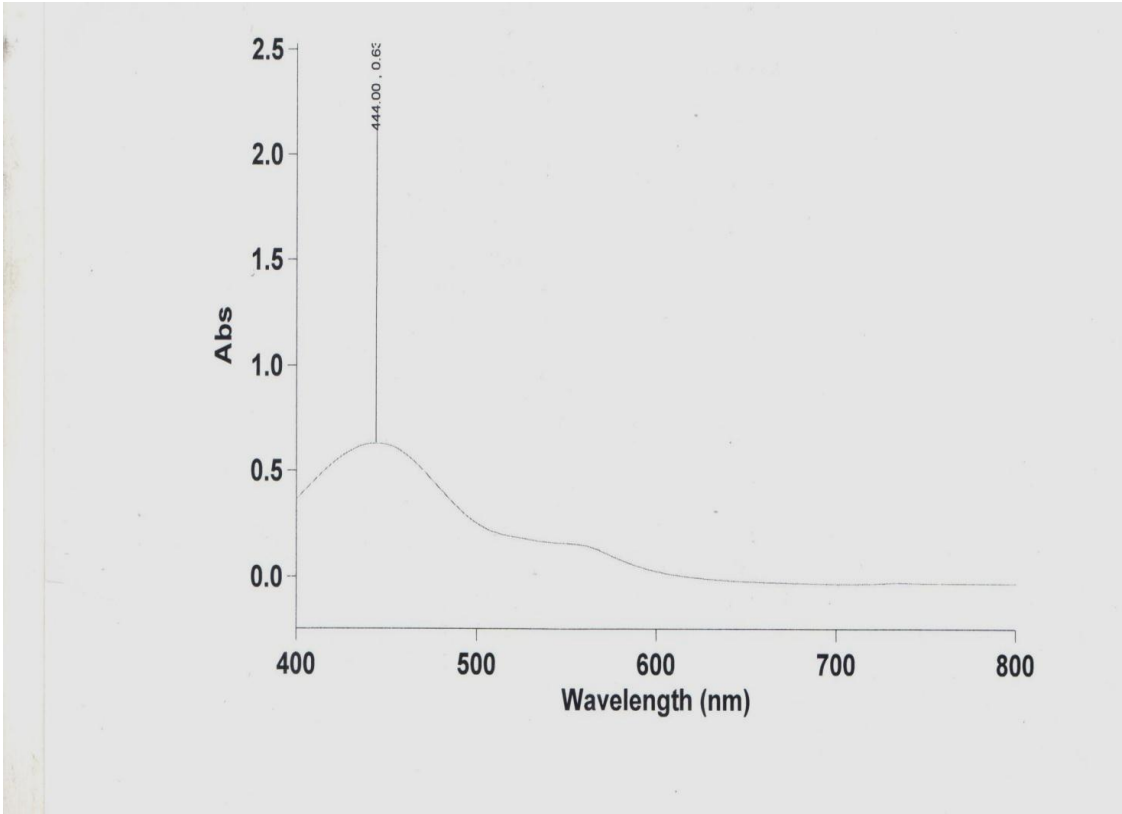
Uv-Visible Result of Dye 3b in Methanol



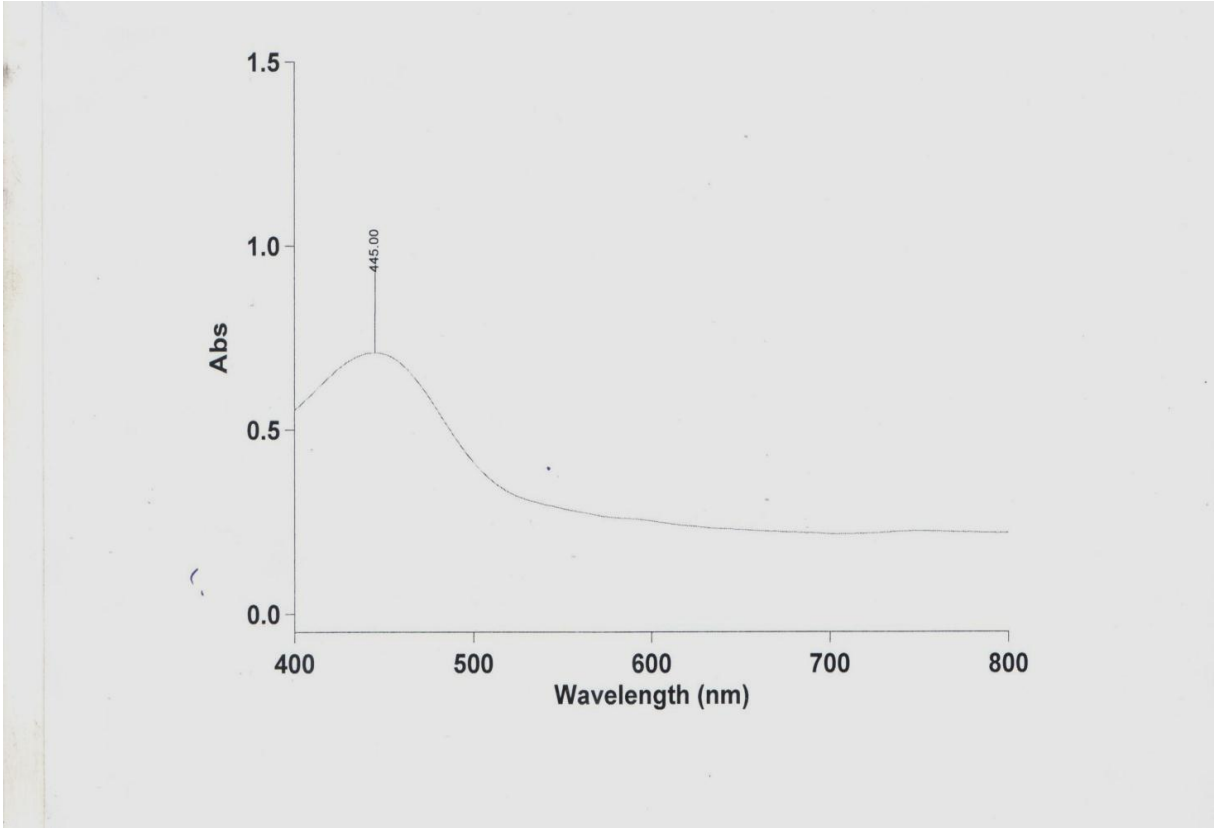
Uv-Visible Result of Dye 3c in DMSO



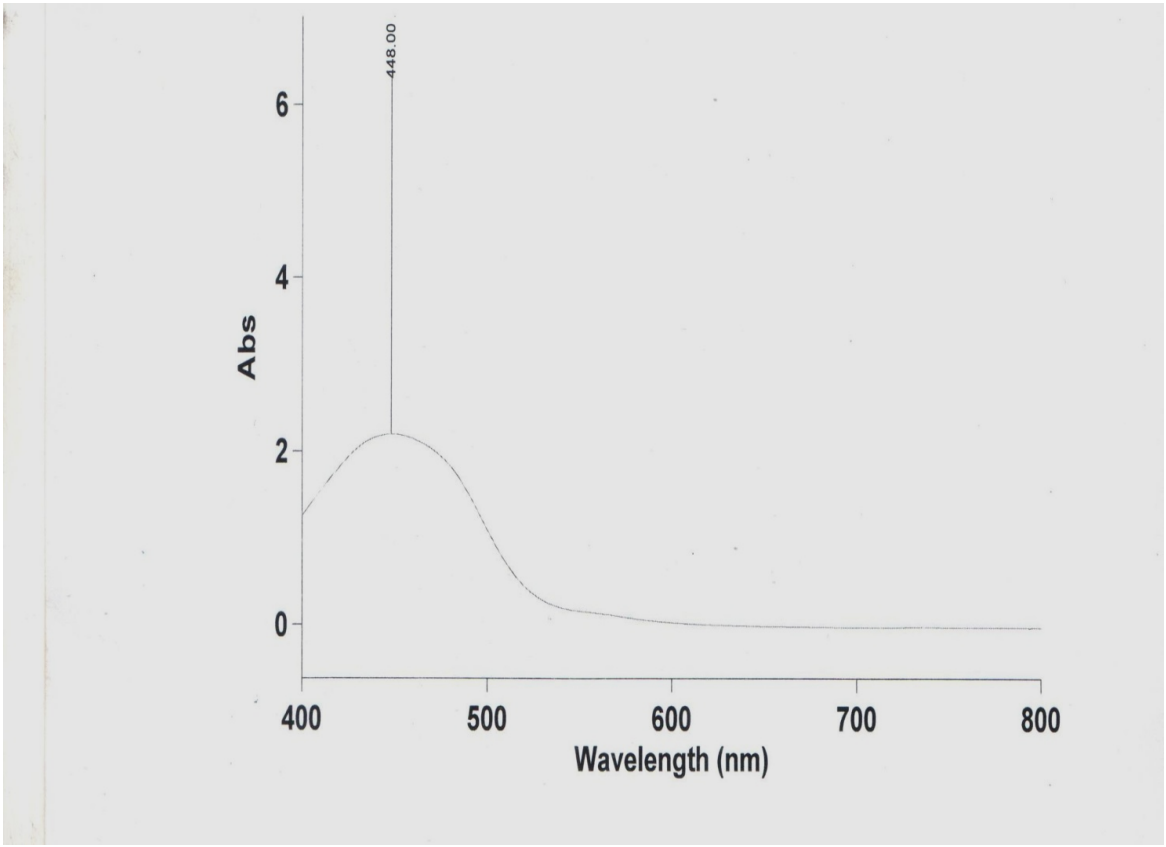
Uv-Visible Result of Dye 3c in Methanol



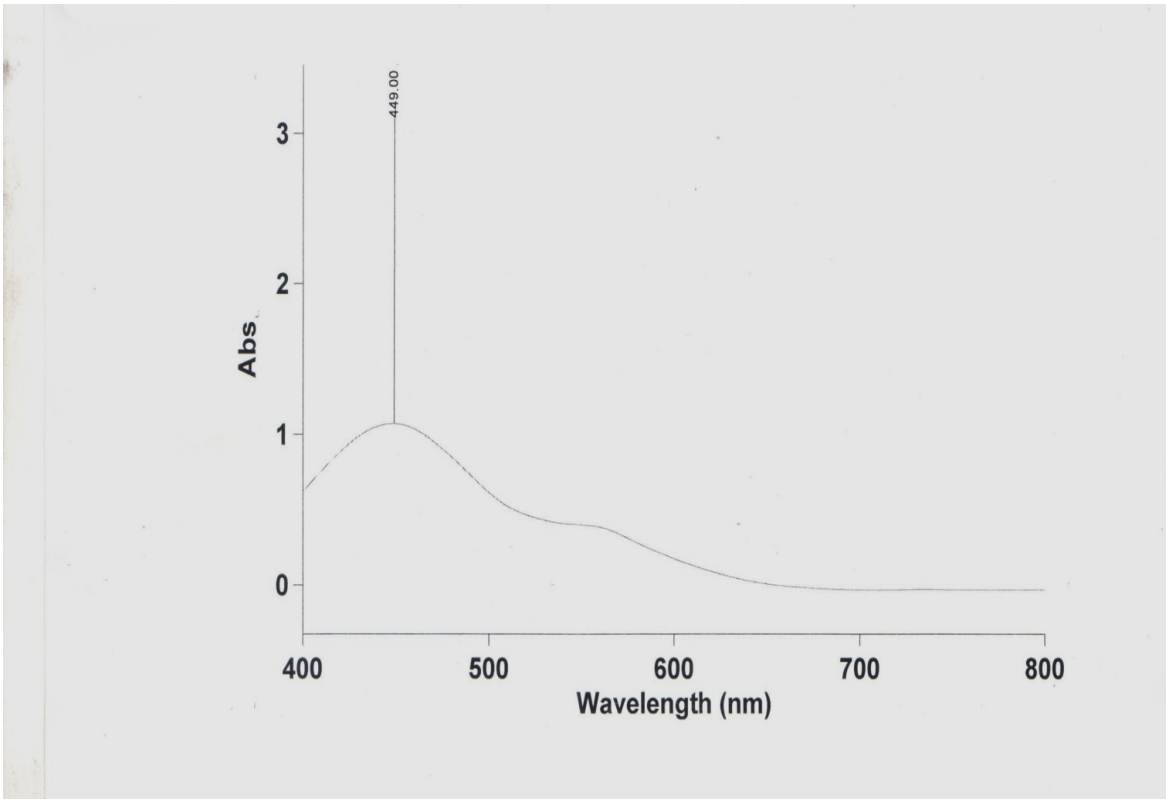
Uv-Visible Result of Dye 4a in DMSO



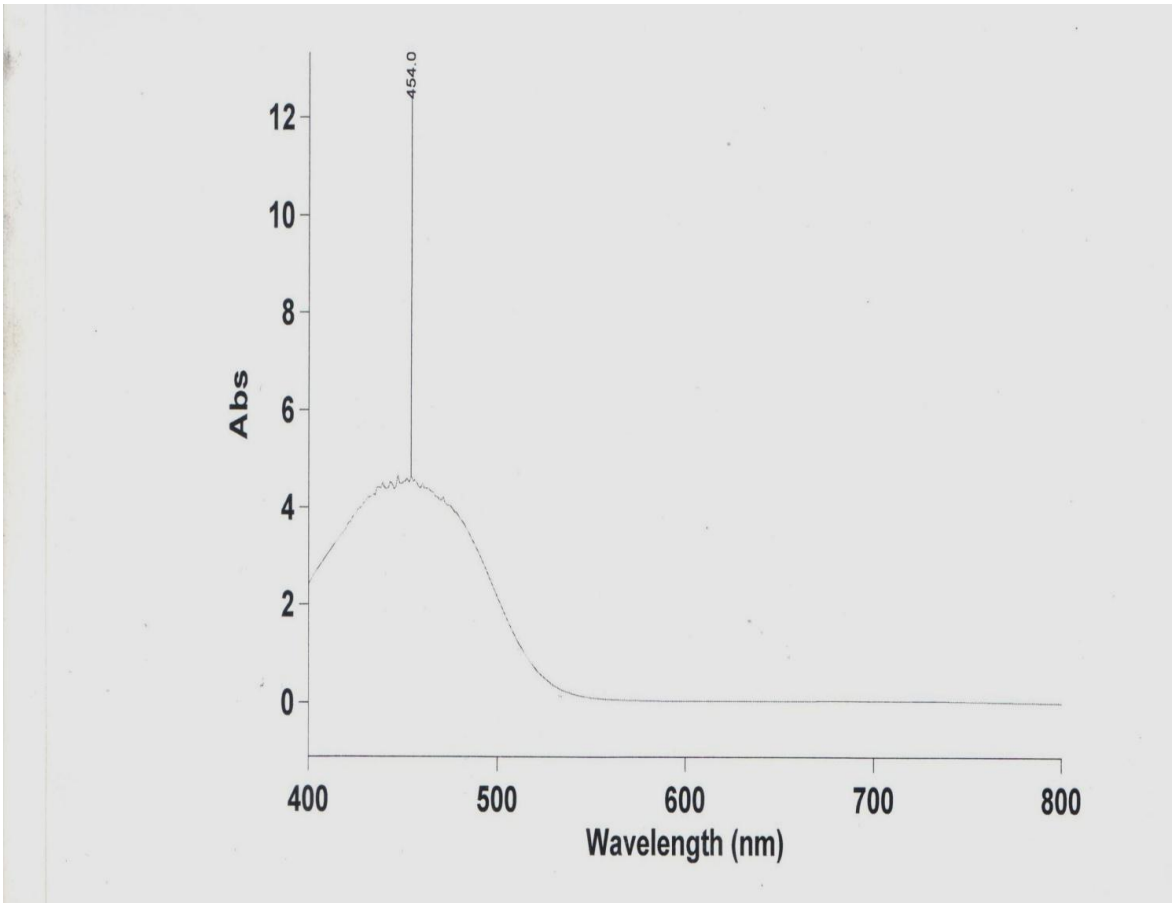
Uv-Visible Result of Dye 4a in Methanol



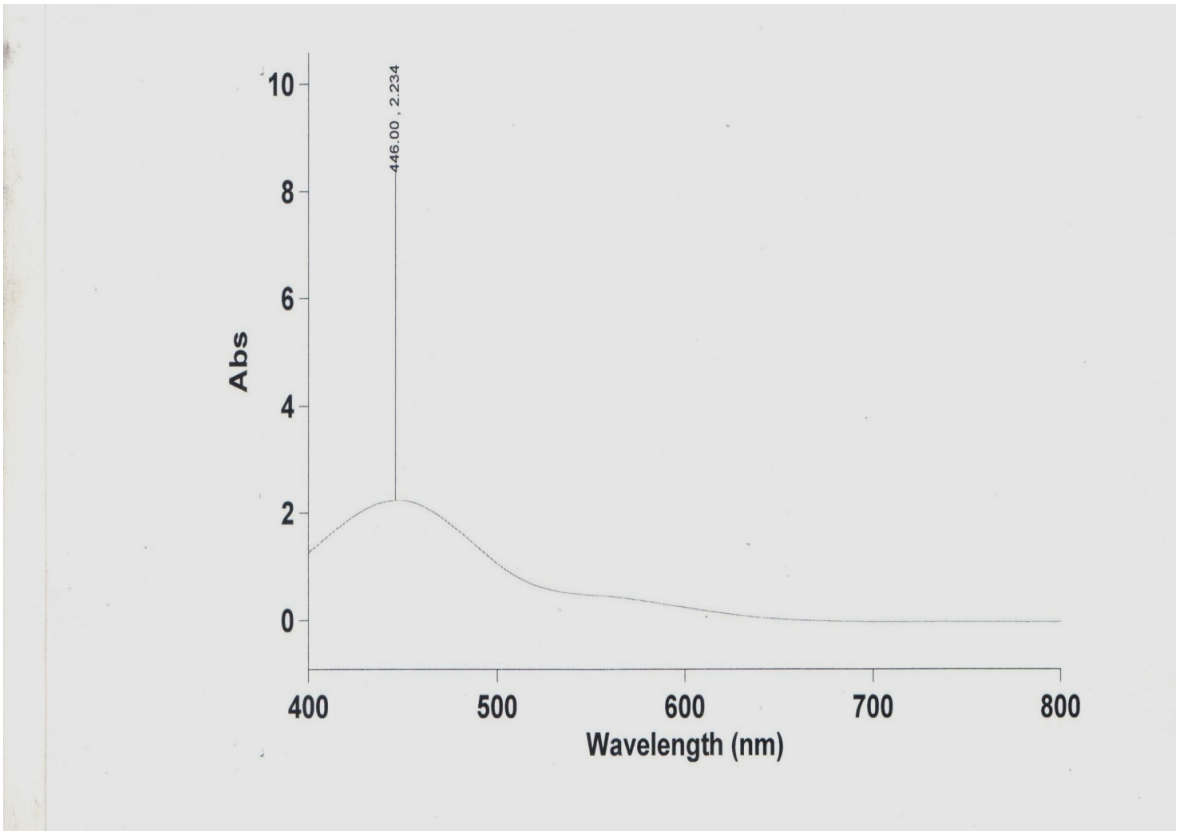
Uv-Visible Result of Dye 4b in DMSO



Uv-Visible Result of Dye 4b in Methanol

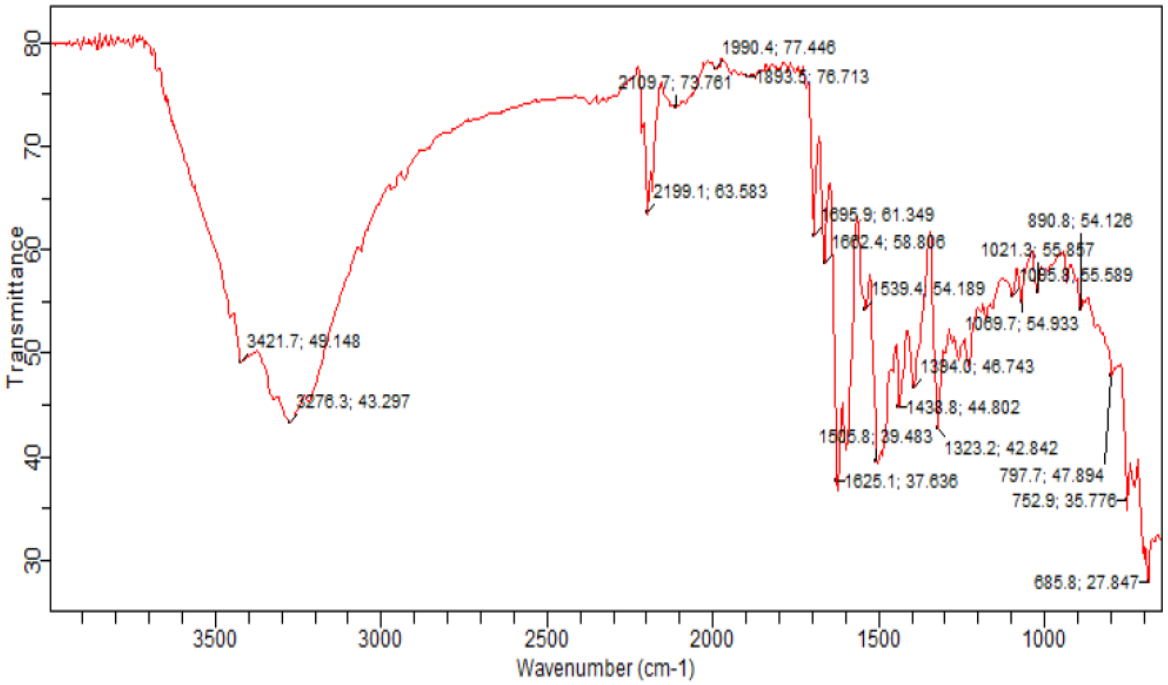


Uv-Visible Result of Dye 4c in DMSO

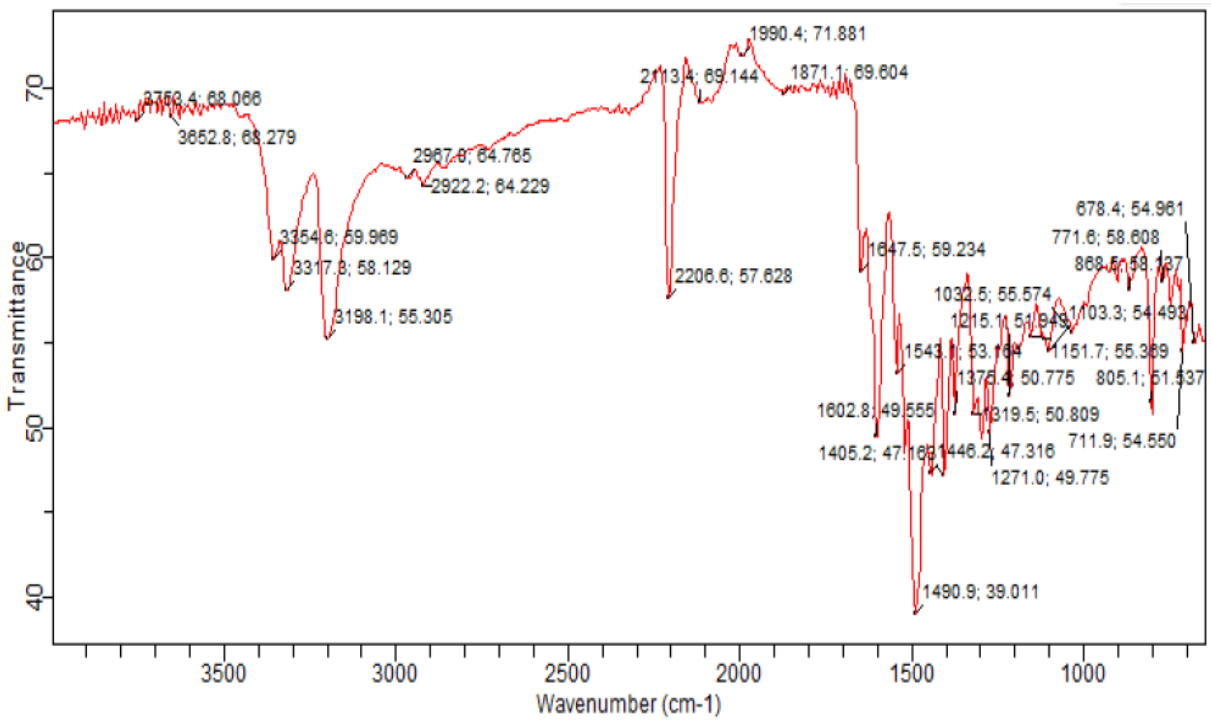


Uv-Visible Result of Dye 4c in Methanol

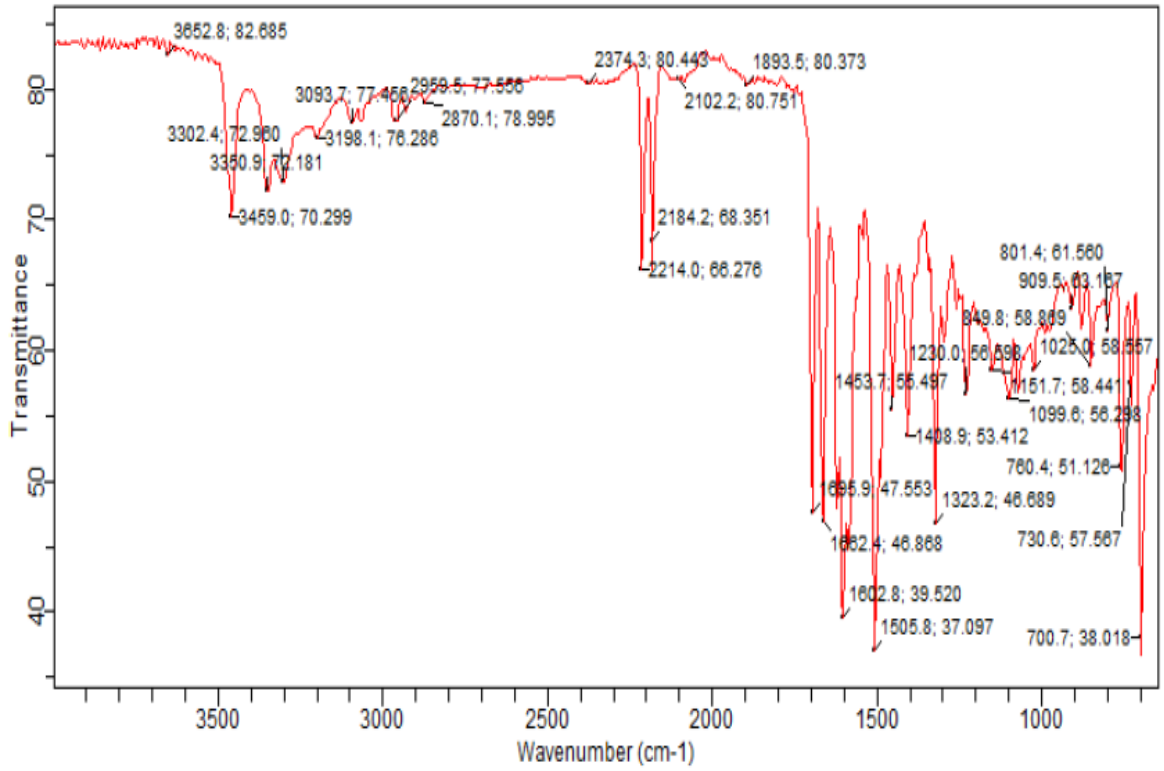
APPENDIX II: INFRA RED SPECTRA OF INTERMEDIATES AND DYES



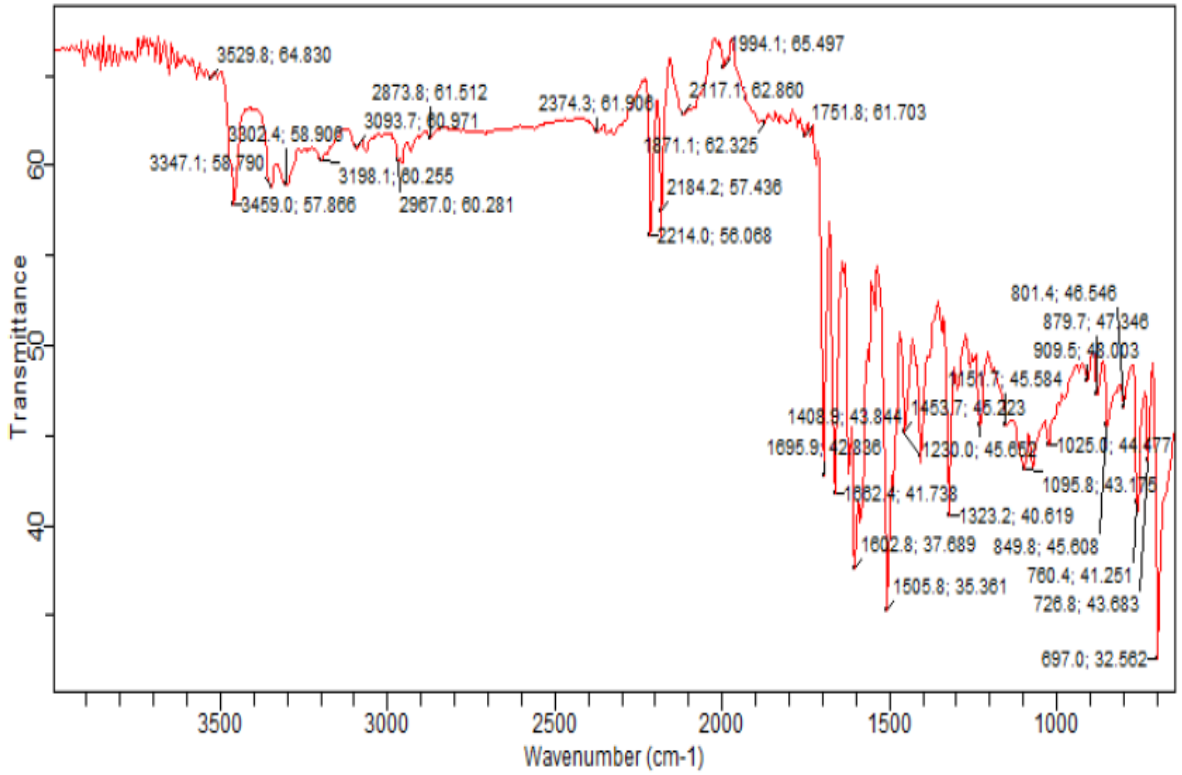
FTIR Result for Intermediate 1



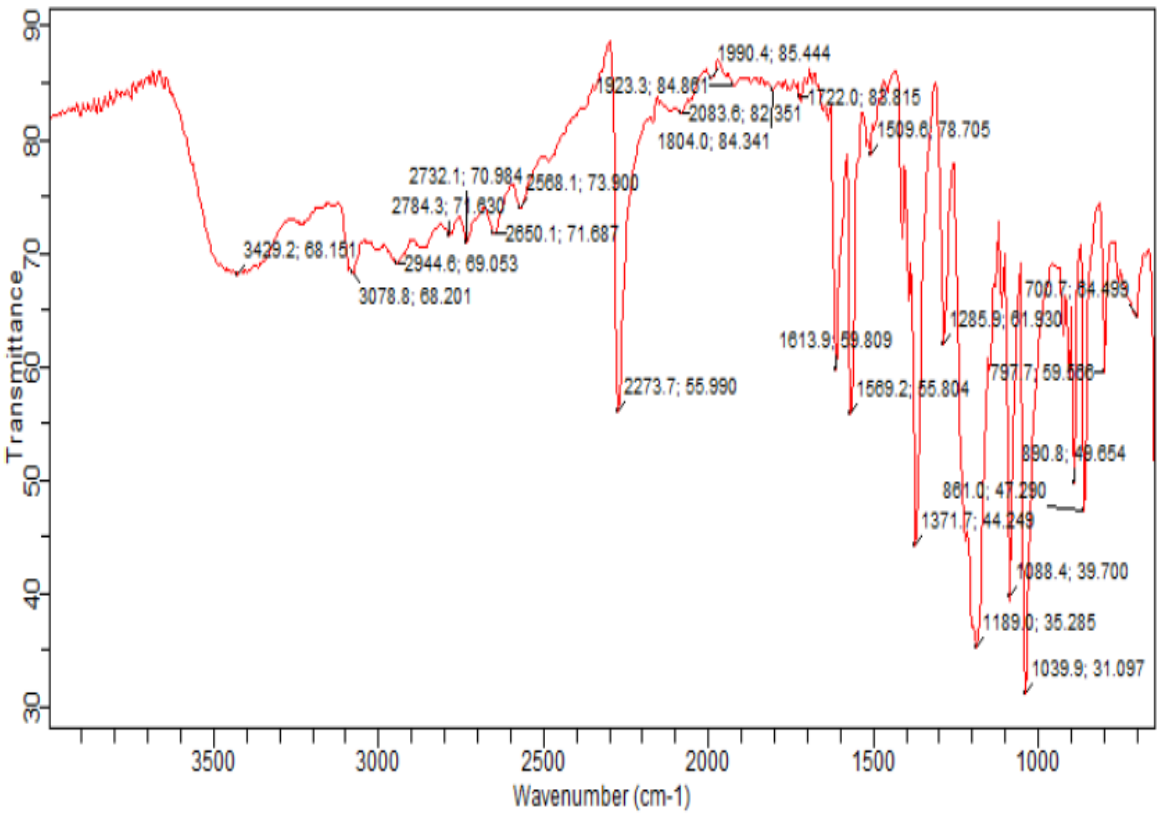
FTIR Result for Intermediate 2



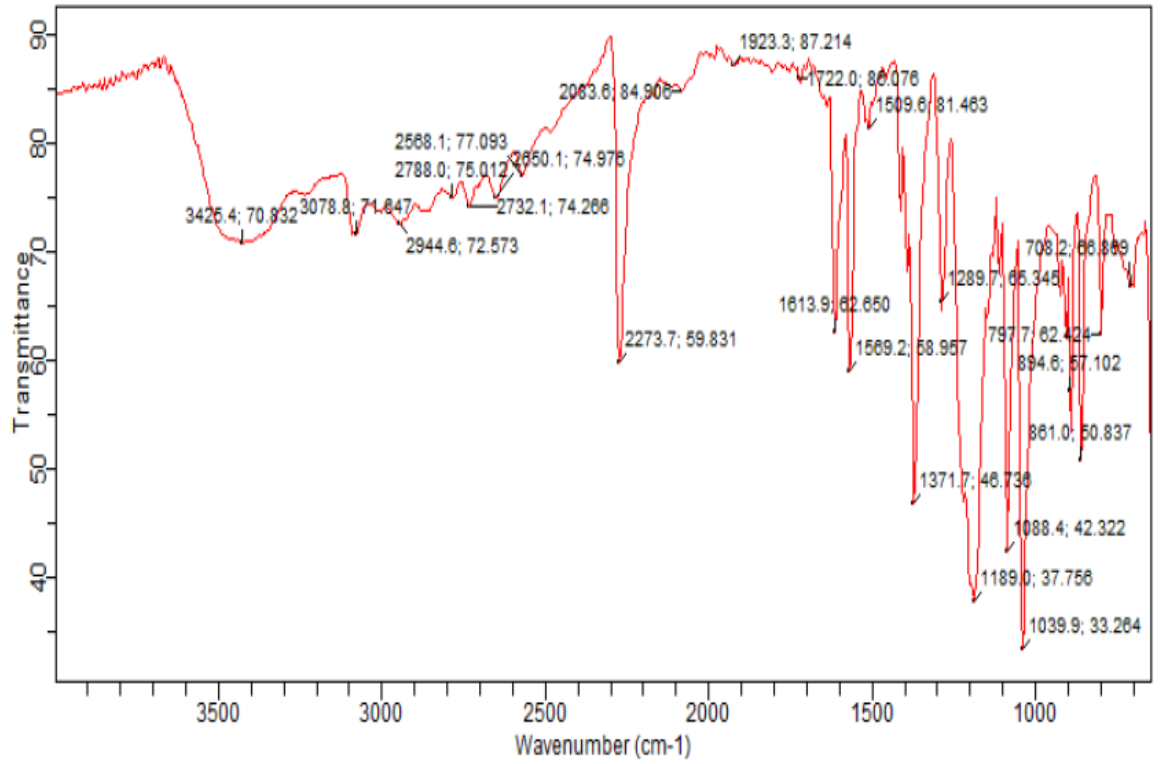
FTIR Result for Dye 1a



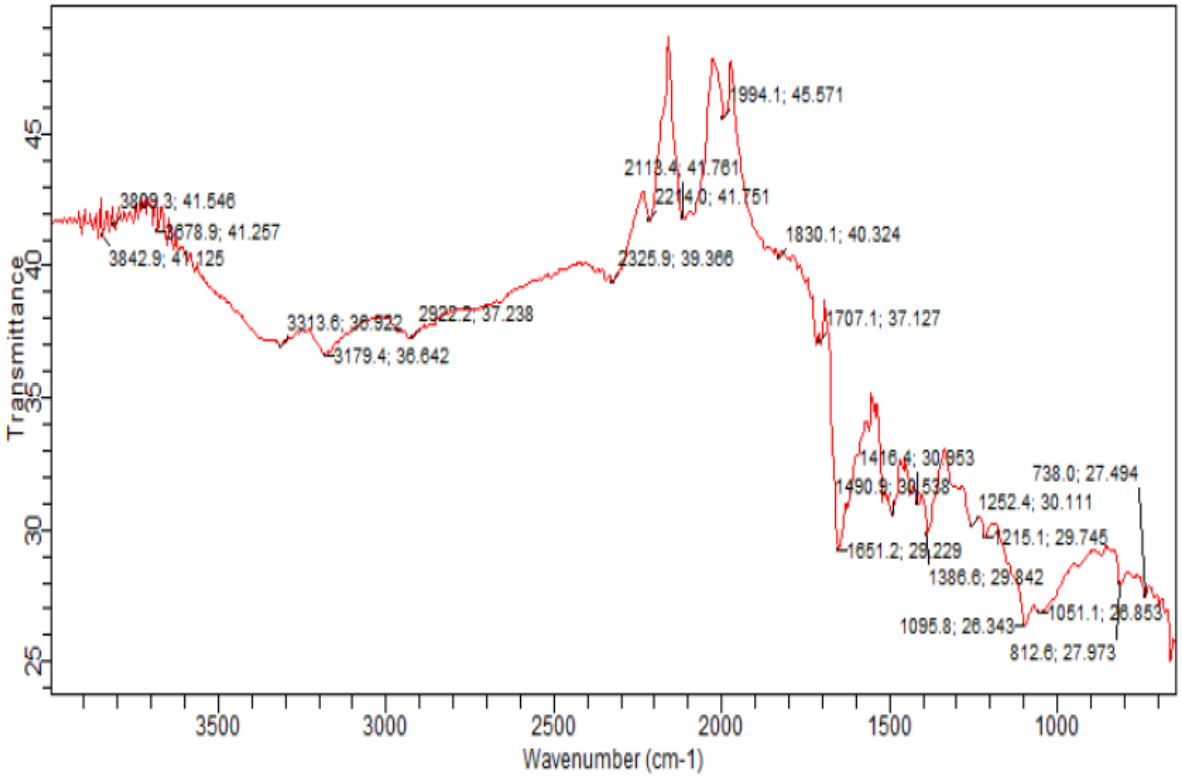
FTIR Result for Dye 1b



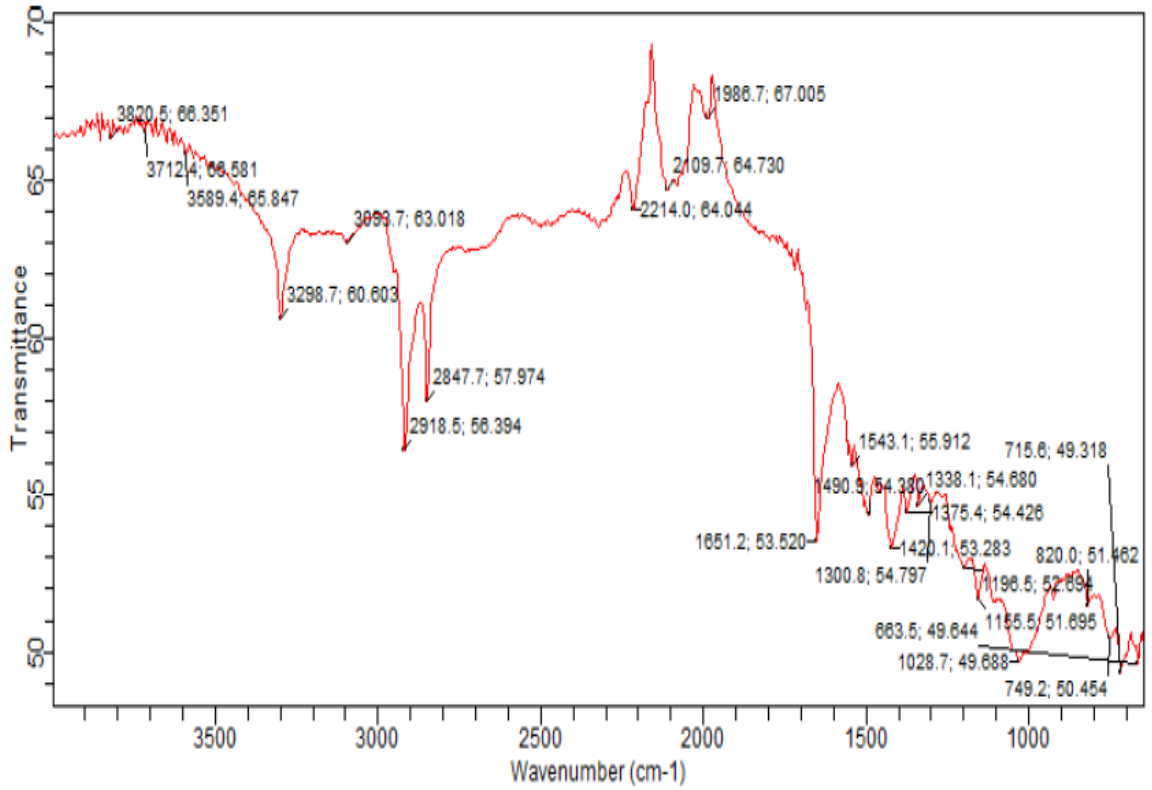
FTIR Result for Dye 1c



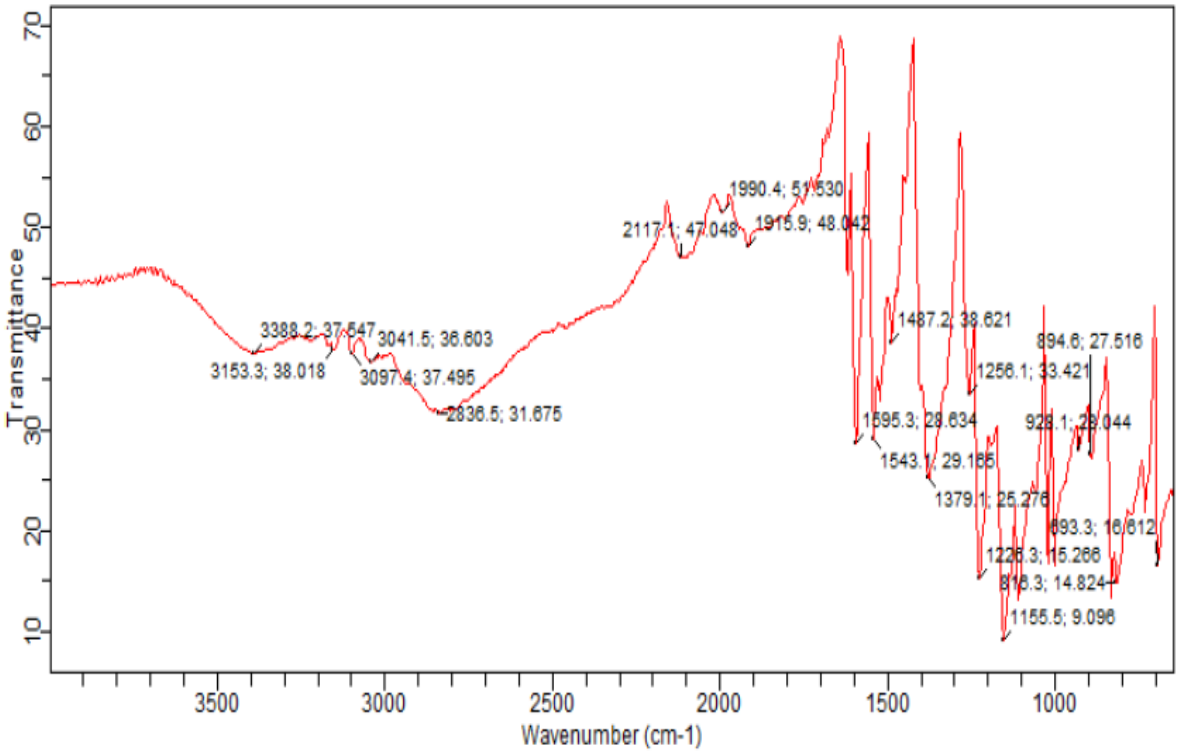
FTIR Result for Dye 2a



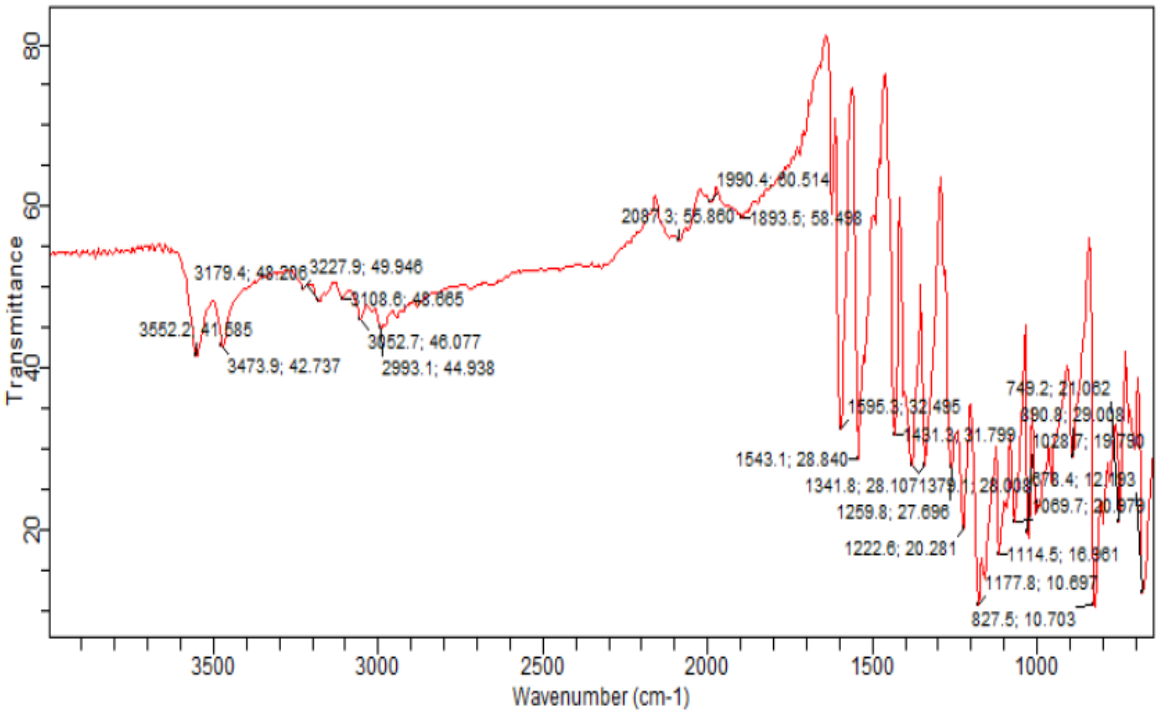
FTIR Result for Dye 2b



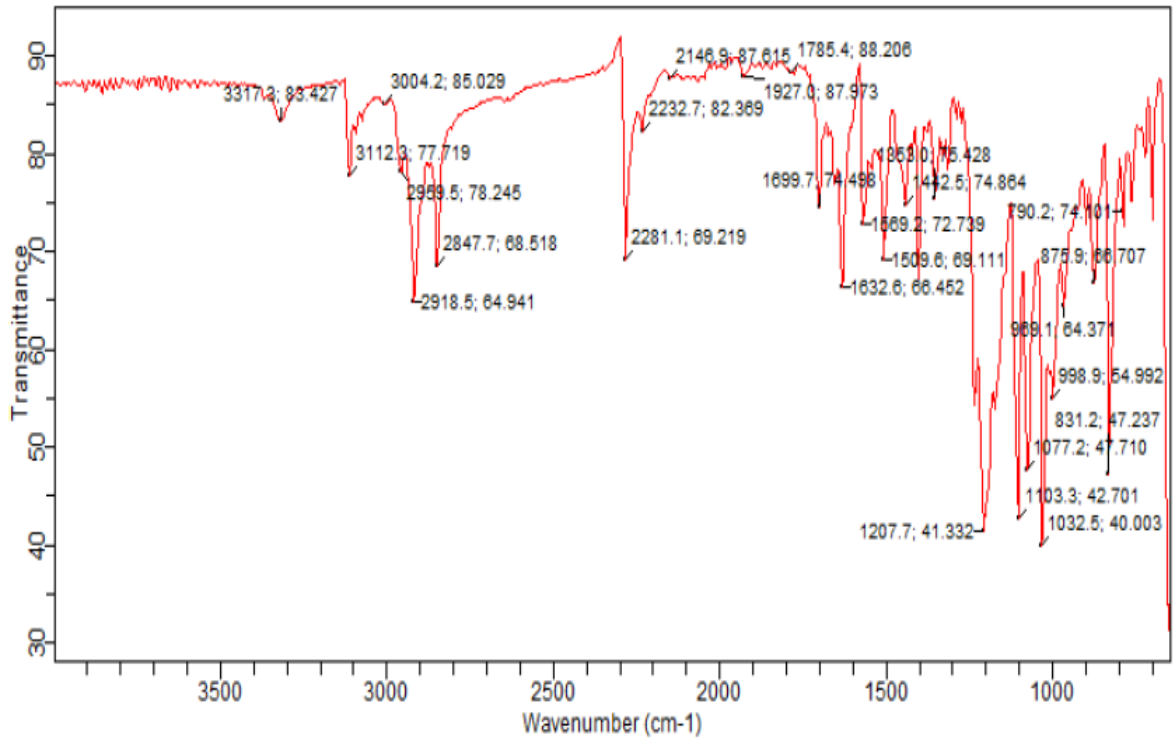
FTIR Result for Dye 2c



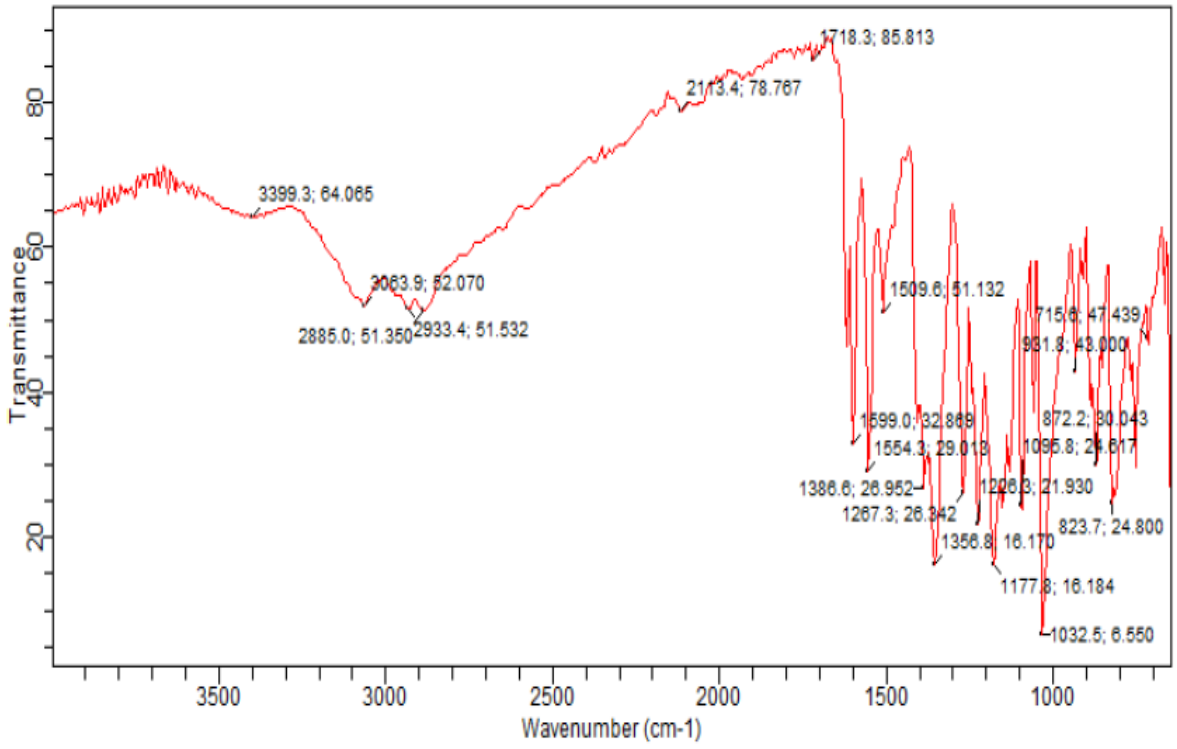
FTIR Result for Dye 3a



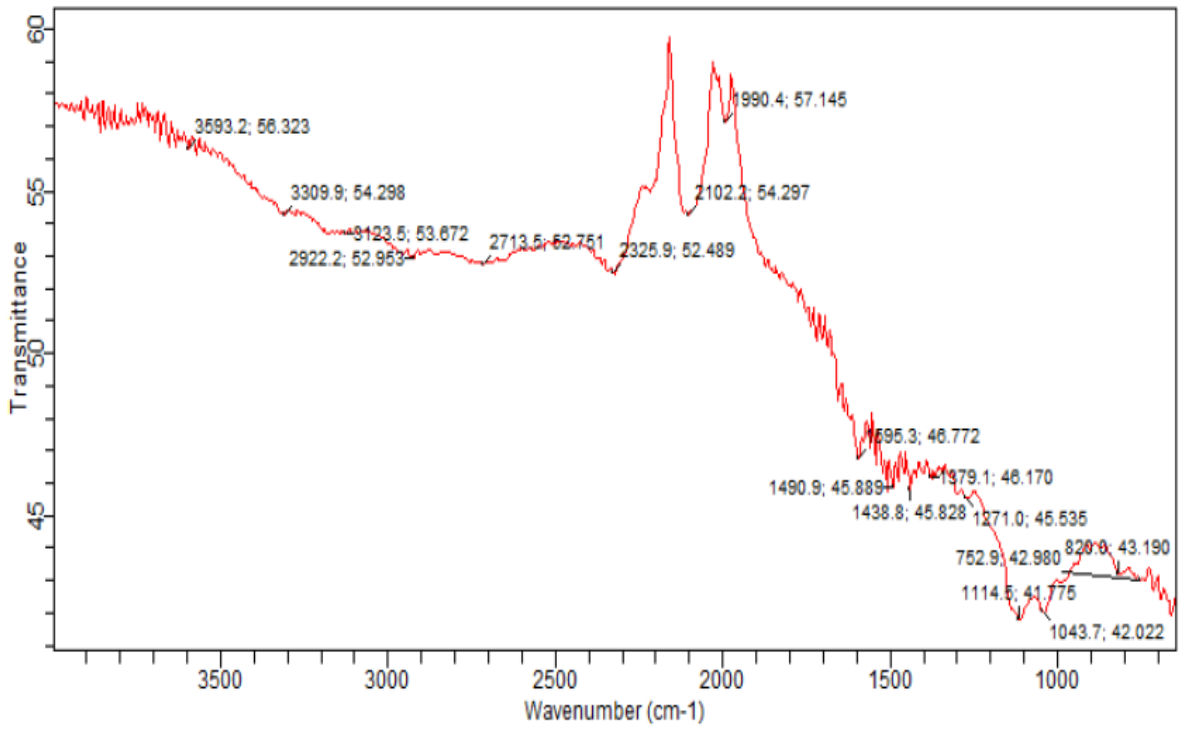
FTIR Result for Dye 3b



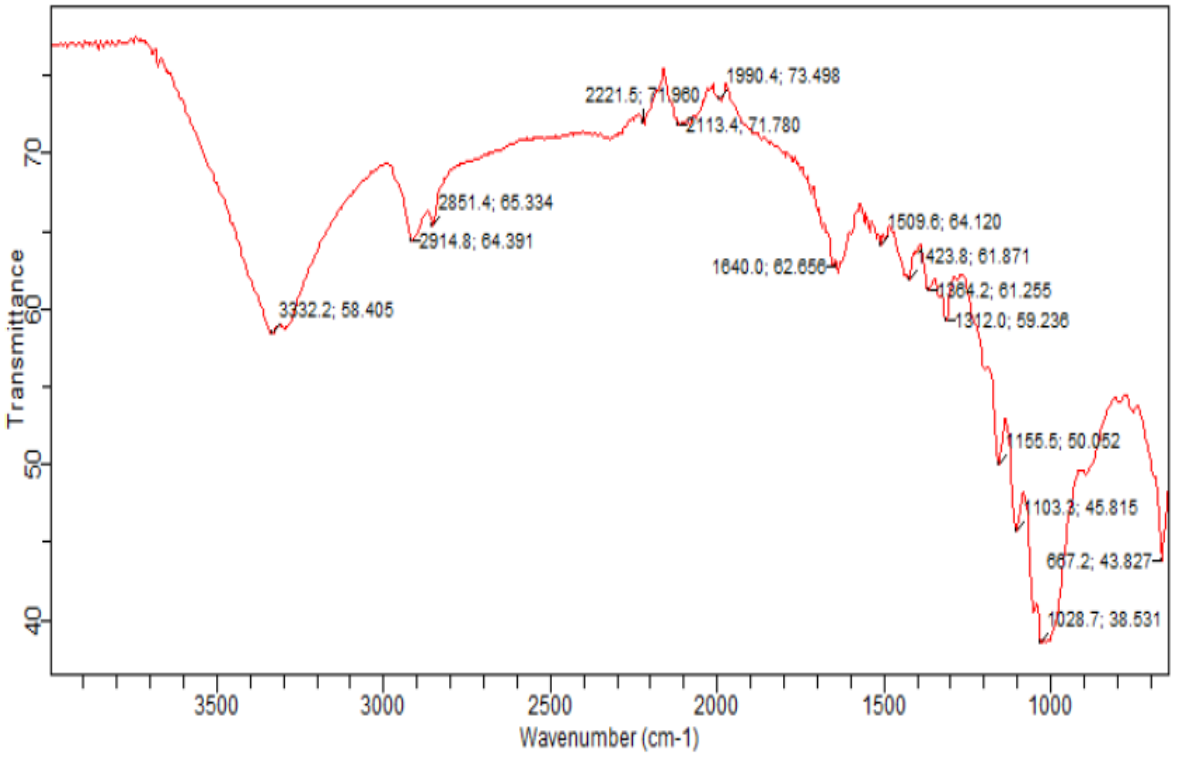
FTIR Result for Dye 3c



FTIR Result for Dye 4a

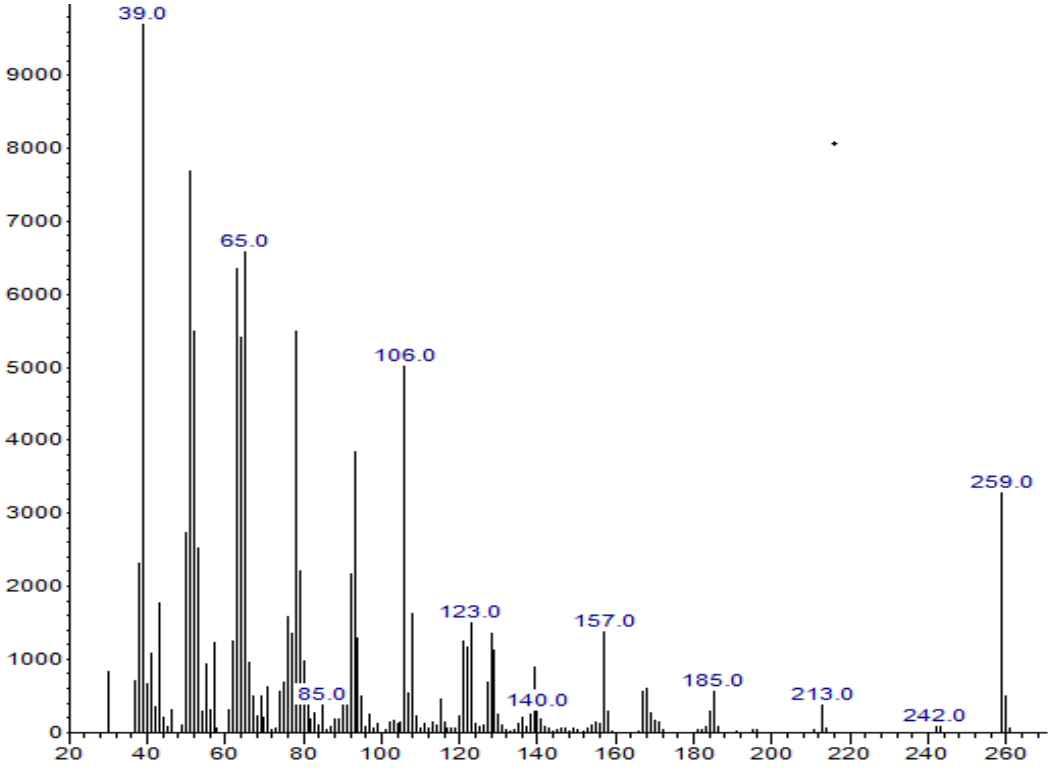


FTIR Result for Dye 4b

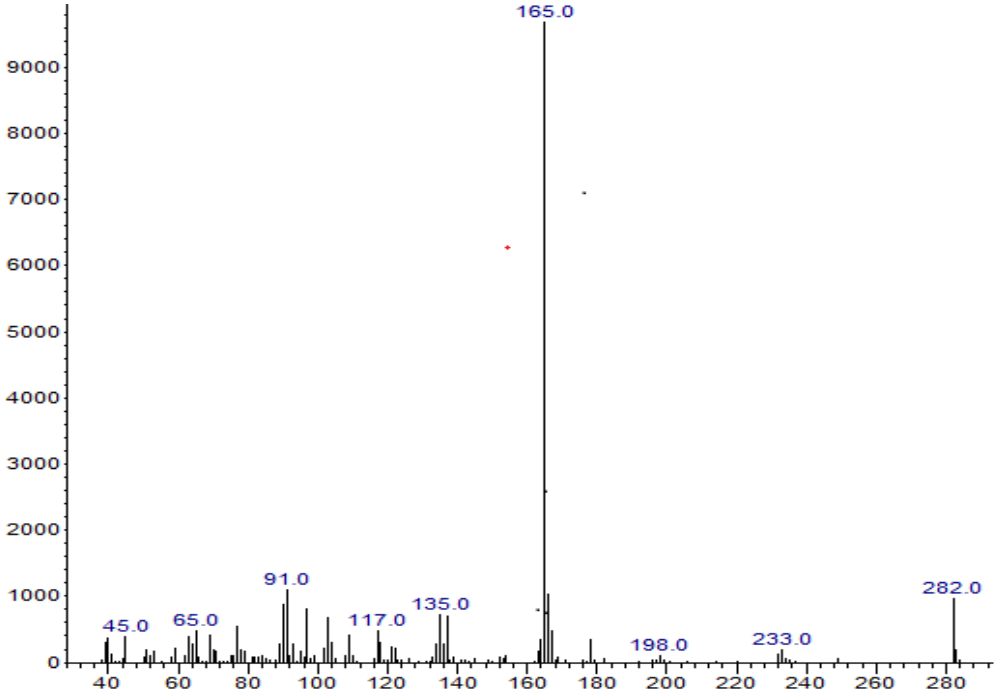


FTIR Result for Dye 4c

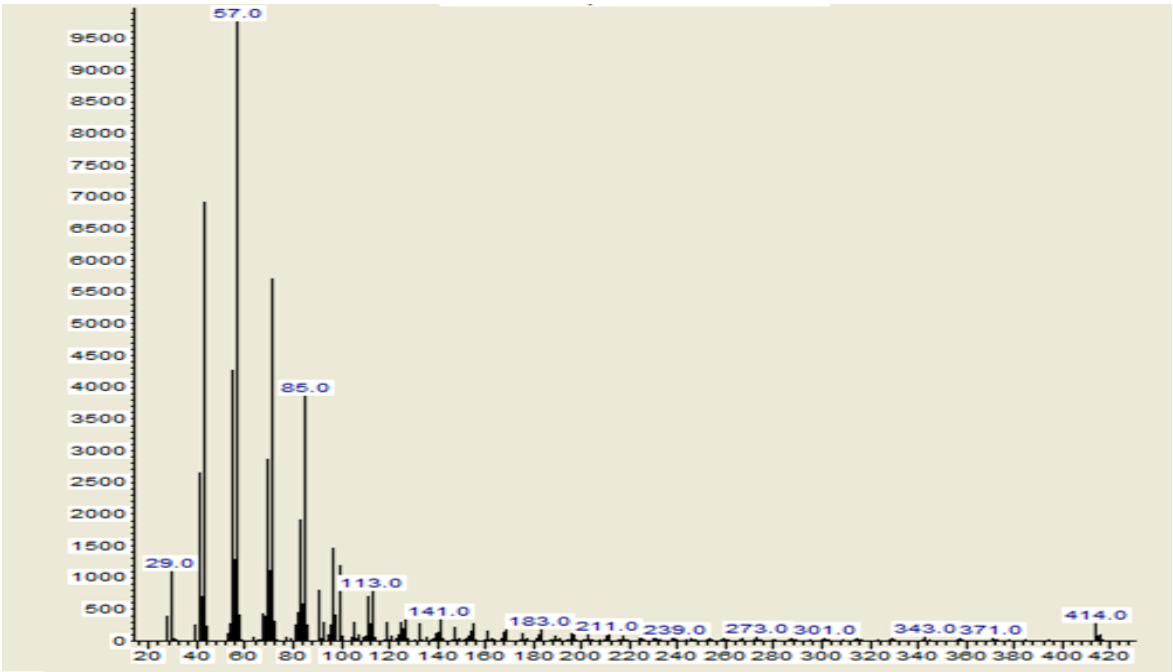
APPENDIX III: GC-MS OF INTERMEDIATES AND DYES



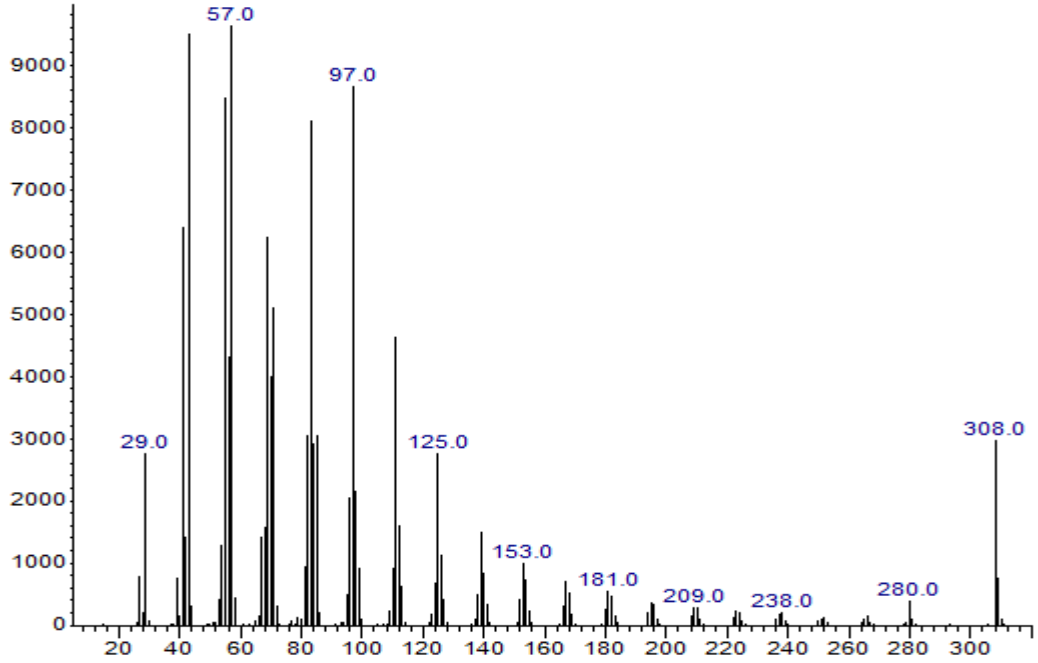
GC-MS Result for Intermediate 1



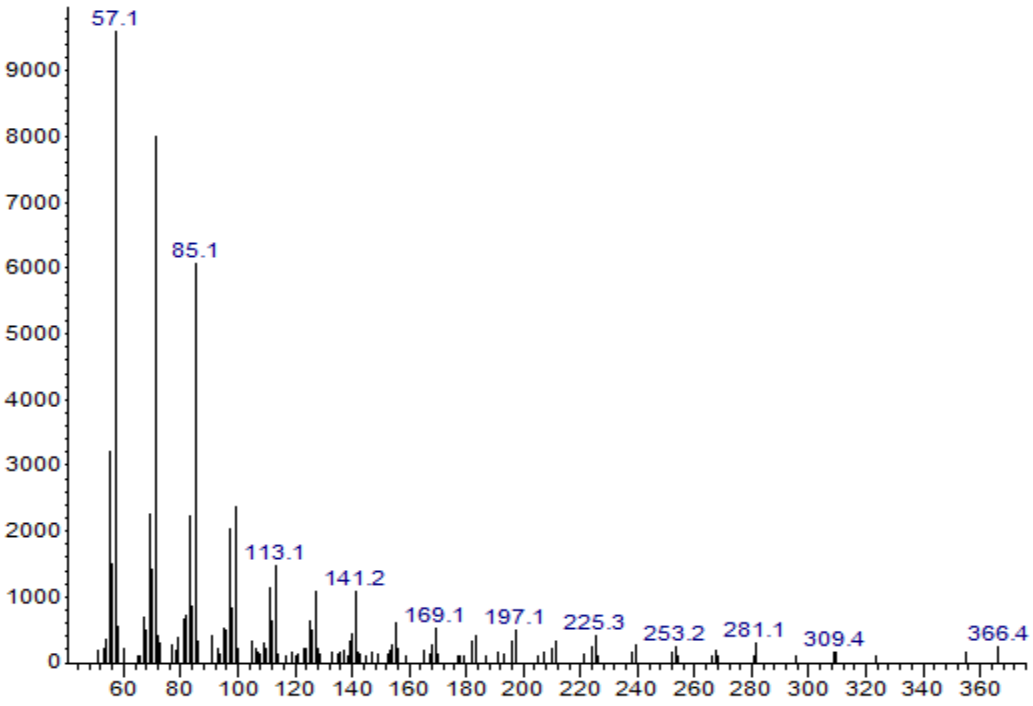
GC-MS Result for Intermediate 2



GC-MS Result for Dye 2a

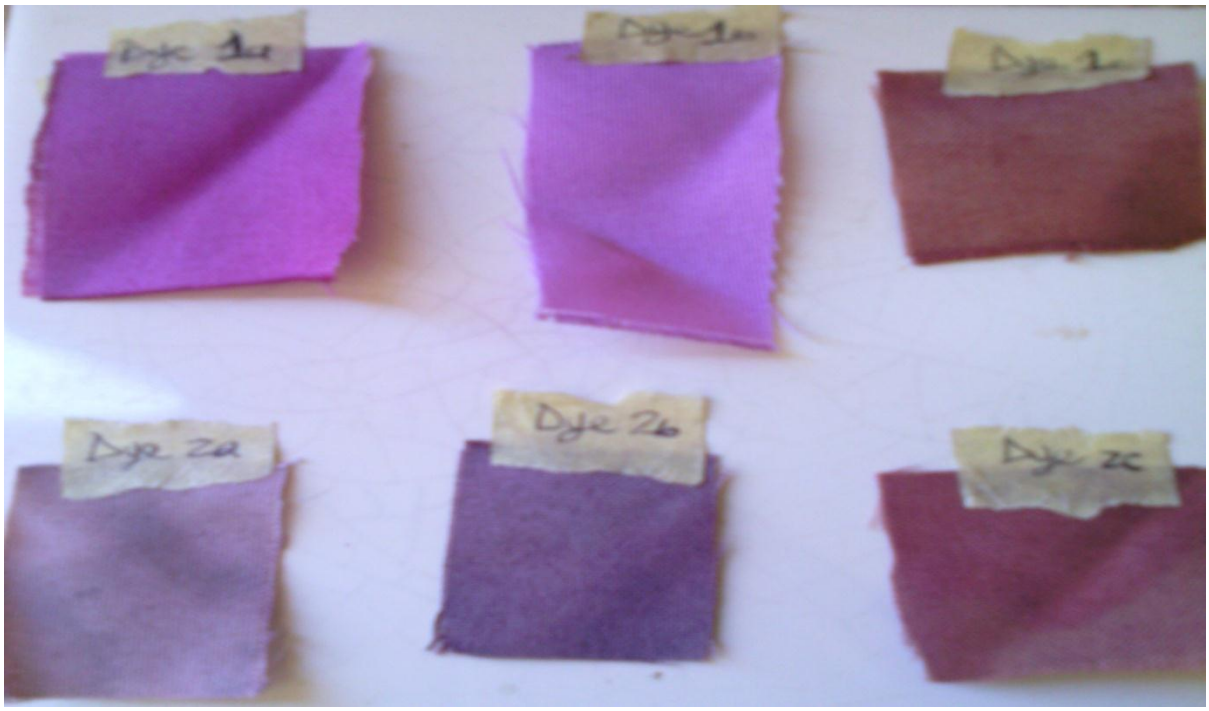


GC-MS Result for Dye 3a

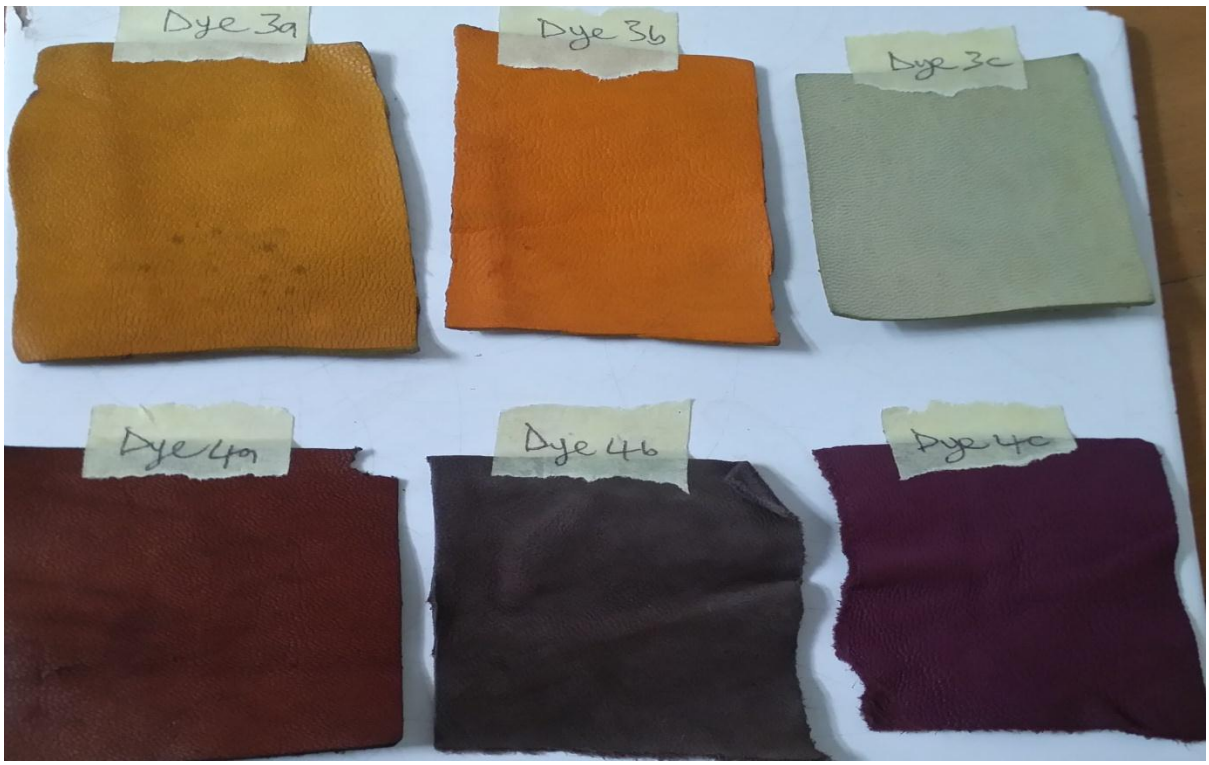


GC-MS Result for Dye 4a

APPENDIX IV: PHOTOGRAPHIC PICTURES OF DYED SUBSTRATES



Photographic Picture of Dyed Polyester Fabric



Photographic Picture of Dyed Chrome Tanned Leather