

**SYNTHESIS AND APPLICATION OF QUARYLUM DYES ON POLYESTER
AND NYLON 6 FABRICS**

By

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MAY, 2017

DECLARATION

I declare that the work in this dissertation entitled “**SYNTHESIS AND APPLICATION OF SQUARYLIUM DYES ON POLYESTER AND NYLON 6 FABRICS**” 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.

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CERTIFICATION

This dissertation entitled “SYNTHESIS AND APPLICATION OF SQUARYLIUM DYES ON POLYESTER AND NYLON 6 FABRICS” by YAKUBU ALI meets the regulations governing the award of the degree of Master of Science in Colour Chemistry and Technology of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research is dedicated to GOD ALMIGHTY for his love and provision over my life all through this programme and to my beloved late father, Mr. Ali London.

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In every man's work, there are those people whose association is of benefit to his success and this work is not an exception of this fact. Therefore, my profound gratitude goes to ALMIGHTY GOD the giver of life and the creator of the universe who has kept my life to this day, and given me the grace to acquire a Masters Degree in Colour Chemistry and Technology in Ahmadu Bello University, Zaria. I sincerely appreciate the efforts of my supervisors Prof. K. A. Bello and Dr. A. Giwa, without whose close supervision, accessibility, patience, understanding and most importantly mentorship, this work wouldn't have been completed. My Parents, Mr. (late) and Mrs. Ali London for their parental care, and love. Also, to all my family members ,especially Mr. Samuel Ali, Mrs. Abigail Ali and Mrs. Justina Solomon who stood by me as a pillar. I must sincerely thank the entire academic and non academic staff of the Department of Polymer and Textile Science for availing me with most of my equipment, Department of Chemistry, Department of Biochemistry, Department of Pharmaceutical Chemistry, ABU, Zaria, for providing me with some chemicals. I must not also fail to appreciate Prof. M. K. Yakubu for providing me with some chemicals and academic support, Prof. A. H. Rafindadi for his financial and academic support, Dr. Habila for his academic support, National Research Institute for Chemical Technology for the FTIR and GC-MS analysis, Mr. Solomon Briska for his financial support, my fiancée, Simi Pam, for her prayers and financial support, and all my friends , Yakubu Iliya, Kumba Samba, Rose Gyam, Naomi Bata, Samuel Adejo, Abolude Isaac, Mr Solomon Briska, Franca, Madam Joyce and Yahaya. Finally, to my Uncle, Mr. James Lamela, for his parental care and financial support, and all those who have helped me in different ways.

ABSTRACT

Synthesis and application of squarylium dyes has been undertaken in order to characterise the synthesised dyes by different spectrometric techniques, (FT-IR, UV-visible and GC-MS), and to study their fastness properties, such as wash, light, perspiration, and hot pressing, on nylon 6 and polyester fabrics. Also, effects of time, temperature, carrier concentration and pH was investigated on polyester and nylon 6 fabrics. The dyed fabrics were generally found to show good (4) to very good wash (5), light fastness of (5) and (6), perspiration (4) and (5), hot pressing (4) and (5) on nylon 6 and good to very good on polyester fabric respectively. The dye-bath exhaustion was found to be between 76 % and 92 % on nylon 6 and 57 % and 85 % on polyester respectively. The percentage exhaustion on nylon 6 was found to be very good to excellent and but on polyester it was found to be good to very good. It can be concluded that squarylium dyes can be applied to nylon 6 and polyester fabrics, but better performance was found on nylon 6 than polyester fabric due to the amorphous nature of nylon 6 compared to polyester.

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CHAPTER ONE

1.0 INTRODUCTION

Dye is a chemical substance which is coloured and has the ability to impart its colour onto a substrate from an aqueous dispersion or solution. The substrate may be a textile fibre/fabric, leather, hair, food or cosmetics. In some cases, materials to be dyed possess affinity for the dye and easily absorb the dye from their solution or aqueous dispersion. Dyes and pigments owe their colour to their ability to selectively absorb light within the visible region of the electromagnetic spectrum i.e., 400-700nm. This ability of a dye/pigment to absorb light of these wavelength ranges derives from electronic transitions between different molecular orbitals in the dye molecule and the wavelengths absorbed depend on the energy difference between the orbitals (Wysecki and Stiles, 1967).

Colour absorbs light in a characteristic way and the unabsorbed light, called the complementary colour, is always reflected. Therefore, as dye/pigment which absorbs light within the blue range (435-480 nm) is seen in day light as yellow, which is the complementary colour of that absorbed (Wysecki and Stiles, 1967).

Table 1: Relation of complementary colour observed to wavelength of light absorbed (Griffiths, 1976)

Colour Absorbed	Wavelength Absorbed (nm)	Colour Seen
Violet	400-435	Yellow-green
Blue	435-480	Yellow
Greenish-blue	480-490	Orange
Bluish-green	490-500	Red
Green	500-560	Purple
Yellow-green	560-580	Violet
Yellow	580-595	Blue
Orange	595-605	Green-blue
Red	605-750	Blue-green
Red + violet	400-435	Green

Since no single wavelength of light correspond to purple colour, a mixture of red and violet must be removed from white to obtain the visual effect of green. So all green dyes will have two absorption peaks, in the region 650 nm and 420 nm.

1.1 Classification of dyes according to use

Textiles dyes are classified by the dyer according to their method of application to textiles fibres, but the chemist uses a different method of classification based on their chemical constitution. To emphasise certain common features of a particular importance in relation to general dyeing behaviour and the wet-fastness of the dyeing, the different application classes of dyes can be treated under groups 1 and 2 (Nkeonye ,1987).

1.1.1 Group 1 dyes

This comprises the following

- i. Acid and metal – complex acids dyes (anionic) for wool, nylon.

- ii. Basic (or cationic) dyes for acrylics

Disperse dyes (non –ionic) for cellulose acetate and synthetic – polymer fibres. All the classes of dye in this group are soluble in water, although disperse dyes are only sparingly soluble. They are absorbed by the fibre from aqueous solution by a reversible process, with two important consequences.

- a) An unlevel dyeing can be made more uniform by extending the dyeing time, and
- b) Dye can be desorbed from the dyed material during wet processing subsequent to dyeing and during washing – off, etc. This means that dyeings of maximum fasteness to wet treatment cannot be achieved with the classes of dye in group 1.

1.1.2 Group 2 dyes

The group 2 dyes can be further divided into four classes A- D

- A) These are dyes which are present in the fibre in the form of large water- insoluble particles. dyeing of high fasteness to wet treatment is obtained with these dyes. In this class are the following dyes type
 - 1) **Vat dyes** .This sub- group include the water- insoluble vat dyes and the solubilised vat dyes
 - 2) **Sulphur dyes**. Include in this group are conventional sulphur dyes, leuco sulphur dyes, solubilised sulphur dyes and condense sulphur dyes.
 - 3) **Azoic dyes**. The application of these dyes is based upon the synthesis of a water- insoluble azo compound inside the fibre.
 - 4) **Ingrain dyes**. This is a small group of dyes, almost all of them based on phthalocyanines, which form insoluble colorants inside the fibre under the prescribed application conditions

5) **Oxidation dyes.** This is the name given to small group of dyes which yield insoluble colorants inside the fibre on chemical oxidation. All the dyes under class A are applied mainly to cellulosic fibres, especially cotton

B) Reactive dyes.

These dyes derive their names from their ability to undergo a chemical reaction with the fibre, being subsequently attached to it by a covalent linkage. In consequence, they give dyeing of high fastness to wet treatments. Reactive dyes are applied to cellulose and to polyamide fibres

C) Mordant (chrome) dyes.

Dyes in this class are applied to fibre in conjunction with a metal salt, which serves as the “mordant” .the dye – metal complex, which forms inside the fibre, exhibits greater fastness than the original unmetallised dye. They are of importance in wool dyeing

D) Pigments

These are water – insoluble colorants which can be introduced into the fibre during manufacture by mixing them with the fibre- forming substance prior to extrusion to form the filaments. This coloration method is called “mass- pigmentation” or “mass- coloration” and is only possible with the man – made fibres. Textile can also be coloured with pigments with the aid of a resin (binder), which polymerises during baking to form a transparent film around the fibres in which the coloured pigment particles are embedded.both natural and man-made fibres can be coloured by this technique, to give dyeing of very high fastness to wet treatments.

1.1.3 Dyeing machines

Textiles materials may be dyed in various forms, the most common being loose stock, yarn and fabric. The form in which a textile is dyed is determined by a number of factors. Thus fibres likely to show dyeing variations from batch to batch, e g wool, may be dyed as loose stock and subsequently spun into yarns. Yarns may also be required to be dyed for special purposes eg weaving on jacquard or carpet looms. Fabric dyeing is the most widely practiced, due to their versatility to customer demands and to changes in fashion. Different forms of textile require different machines in order to achieve the best results. In a dyeing machine, dye liquor must pass continuously over the surface of the fibres being dyed, and the necessary movement is achieved in either of three ways

- I. By circulating the liquor through the stationary material
- II. By moving the material through the liquor
- III. By moving both the material and the liquor

In machine where the liquor is circulated, the rate of flow should be high as possible without damage to the material being dyed, as the rate of dyeing is higher at high speeds of liquor circulation. Other important features of a dyeing machine, in addition to pump or propeller, include a heating device (steam heating is most common) a temperature control device (manual or automatic) ,water-inlet and outlet valves and a dye storage tanks.

1.1.4 Factors that affect the choices of the dyestuffs

1. Cheap
2. Non- toxic
3. Compatible to other dyes and chemicals
4. High color strength
5. Better bridgtness
6. Better fastness
7. Good levelness on the materials

1.2 Statement of the Research Problem

The application of squarylium dyes onto substrates is very difficult because of reduced solubility and crystalline nature of the dyes. An attempt to apply the synthesised dyes on textile substrates was undertaken in the present study.

1.3 Justification

Although several works have been done on squarylium dyes, as infra-red dyes, little work has been done on the application of squarylium dyes on textile substrates. This study is an attempt to study the application conditions for the squarylium dyes on polyester and nylon 6 fabrics.

1.4 Aim and Objectives of the Research

1.4.1 Aim

The aim of this work is to synthesize squarylium dyes derived from squaric acid (3-4-dihydroxycyclobut-3-en-1-2-dione), and study their application on polyester and nylon 6 fabrics.

1.4.2 Objectives

The specific objectives of this research include:

- i. To synthesise squarylium dyes from squaric acid (3-4-dihydroxycyclobut-3-en-1-2-dione)
- ii. To characterize the dyes using FTIR, UV-spectrophotometer and GC-MS
- iii. To investigate the application of the synthesised dyes on polyester and nylon 6 by varying time, pH, temperature and carrier concentrations.
- iv. To determine the % exhaustion of the dyes
- v. To determine the fastness properties of the dyed fabrics.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Squarylium Dyes

Squarylium dyes are a class of organic dyes showing intense fluorescence, typically in the red and near infrared regions. Their absorption maxima are found between 630 and 670 nm and their emission maxima are between 650–700 nm, (Saito *et al.*, 2006). Squarylium dyes are a family of chromophores containing structures such as cyanine dyes, two donor groups conjugated to an electron deficient oxocyclobutenolate core, leading to a highly electron delocalized structure that can be exemplified as zwitter ion (Yuanwei, 2008). Generally, squarylium dyes with donor-acceptor-donor structures are synthesised by the condensation reaction of 3, 4-dihydroxy-3-cyclobutene-1, 2-dione (squaric acid) with activated aromatic or heterocyclic components. In 1965, Treibs and Jacob obtained a red-violet solid when they reacted squaric acid with pyrrole, which is the first report related to squarylium dye synthesis. Later, this class of dyes was named “squarylium” by Schmidt (1967). Since then, numerous studies have been reported in 1990s on squarylium dyes, covering various areas from synthetic methods and reaction mechanisms to physical properties. Due to their zwitter ionic properties, squarylium dyes exhibit strong absorption ($\epsilon > 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$) and emission in the near-IR region. They are characterized by their unique aromatic four member ring system derived from squaric acid. (3, 4-dihydroxycyclobut-3-ene-1, 2- dione), (Saito *et al.*, 2006).

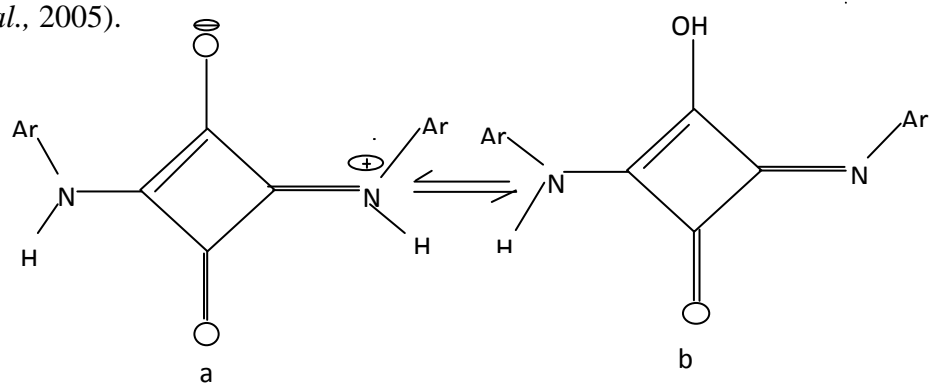
This class of cyanine dyes is distinguished by their good photochemical stability and sharp absorption with high extinction coefficients in solution in the red and near IR region (Keil and Hartmam, 1991).

Squarylium dyes have poor solubility in most solvents, except for dichloromethane and a few others. While many of these dyes are sparingly soluble in most common solvents, the solubility is, to some extent, an important criterion for the use of these squarylium dyes in near-IR region (Hwang *et al.*, 1998).

The squarylium dyes have found many uses as functional dyes. Functional applications include their use as near-infrared absorbers (*e.g.* for optical data recording materials), laser dyes, light filters, photoconductive materials, long wavelength fluorescent labels and as dichroic dyes for liquid crystal displays (Soo-Youl *et al.*, 2005).

The squarylium dyes are conventionally used as a charge generating material for an organic photo conductor. squarylium dyes are applied to an organic light-emitting diode because it shows efficient red luminescence (Yanagi and Hwang, 2007).

X-ray crystallographic analysis of these dyes demonstrated the special delocalized nature of the π -electron system, tautomerism occurs when the amino group is secondary (Soo-Youl *et al.*, 2005).



Keto- enol tautomeric forms of squarylium dye

Figure 2.1: kenol –enol tautomeric forms of squarylium dyes

2.1.1 Symmetrical Squarylium Dyes

The starting raw material for squarylium dyes synthesis, is squaric acid (3,4-dihydroxy, cyclobut-3-ene-1,2-dione), which is a colourless solid at room temperature, which was first synthesised by (Cohen and coworkers 1959), Shortly after the first synthesis of red-violet squarylium dye from the condensation of squaric acid and pyrroles, by (Treibs and Jacob 1965; Ziegenbein and Sprenger, 1966) added more structures to the squarylium family by replacing pyrrole with azulene and dialkylaniline. These condensation reactions were carried out in n-butanol/benzene mixed solvent, meanwhile the water generated was removed from the refluxing system by azeotropic distillation, and this protocol later became a classical way for synthesizing symmetrical squarylium dyes. Under these reaction conditions, the condensation mechanism was suggested by (Ziegenbein and Sprenger, 1966), since the first report of squarylium dyes, their derivatives have been prepared by condensation of aryl or heterocyclic compounds with squaric acid, this showed which kind of squarylium dyes are possible to prepared. Jyothish *et al.*, (2004), showed recently that one can achieve semi-squarylium and unsymmetrical squarylium dye depending on the electronic properties of the donors. For example, the quinaldium scaffold with electron-withdrawing groups (Br, I, CN and NO₂) make the heterocyclic ring electron deficient and the symmetrical squarylium dye was obtained (Yuanwei, 2008).

2.1.2 Unsymmetrical Squarylium Dyes

According to structure of squarylium dyes, they can be classified into two groups, symmetrical and unsymmetrical squarylium. Symmetrical squarylium have the same electron-donating groups on each side of the oxocyclobutenolate core, so the synthesis involves 2 equivalents of electron-rich aromatic or heterocyclic compounds and 1

equivalent of squaric acid. Upon refluxing in n-butanol/benzene mixture, symmetrical squarylium can be obtained with high yields. Unsymmetrical squaryliums, however, have different electron-donating groups on each side, thus the preparation is more complicated. In general, the synthesis and separation of the semi-squarylium intermediate is required and crucial in order to form unsymmetric squarylium dyes. There are two synthetic routes to afford unsymmetrical squarylium dyes, and both start from derivatives of squaric acid. The first strategy is using thionyl chloride or oxalyl chloride to prepare 3,4-dichloro-cyclobut-3-ene-1,2-dione, then reacting this with one equivalent of an activated aromatic compound, followed by immediate hydrolysis to obtain the intermediate semi-squarylium, Then the semi-squarylium was allowed to react with a different aromatic compound and afford the final unsymmetric structure. For the past two decades, the synthesis of unsymmetrical squarylium dyes has increased opportunities for squaryliums to be used for industrial as well as scientific purposes. It has been established by the stepwise synthesis *via* intermediates, mono-substituted squaric acids (half units of the dyes).

2.2 Application of Squarylium Dyes

2.2.1 Environmental application of squarylium dyes for detection of heavy metals

The soil and water pollution by the mass quantity of industrial waste which has been caused by rapid industrial development and growth of population have become one of the main social problems. Especially, the pollution by harmful heavy metal ions discharged from the factories is the most serious one. It is well known that many heavy metal ions among the pollutants are not decomposed and accumulates continuously and finally it is impossible to be extracted out fully. Furthermore, the metal ion absorbed into a body not only reduces the body metabolism but also causes harmful effect when

the ion is accumulated over certain level. Copper, among various heavy metals, is an important element in many industrial processes and is an essential inorganic substance. However, it damages liver cells, causes various diseases and obstructs growth of many crops (Ock *et al.*, 2001).

Selective sensing and probing metallic ions is important in biological condition, such as sensing Na^+ , K^+ , Ca^{2+} , and Zn^{2+} . And detection of transition heavy metal ions like Cd^{2+} , Cu^{2+} , Pd^{2+} , Hg^{2+} and Ag^+ is also crucial for industrial and environmental applications. Organic chromophores have been used as indicating units for a long time due to their intense and sharp absorption and emission. Signals can be generated from the chemo sensors when interacting with metal ions and the changes in optical properties can be achieved by electron transfer, energy transfer, and formation of excimers (Yagi and Hiroyuku, 2002) reported a bisquarylium dye and metal coordination studies that showed an exclusive interaction with transition metal ions with a hypsochromic shift in the absorption spectrum.

Fabricated Cu ion sensor using a squarylium dye containing polymeric thin-film. Using surface plasmon resonance method (SPR). The SPR method was used as a signal amplifier to achieve high sensitivity and large linear dynamic range for detection of Cu^{2+} ion. High selectivity to Cu^{2+} ion was obtained by the effective electro-static interaction between squarylium dye and Cu^{2+} ion in the polymeric film.

SPR method is a suitable optical technique, which can effectively monitor the interaction between squarylium-dye and Cu^{2+} ion. SPR technique is well-known signal transducing principle that can convert the chemical signal caused by the interaction between the analyte and recognition material to the useful optical signal. Its optical signal may appear as the refractive index change and/or the thickness change in the

polymeric film. In the case of the polymeric ion sensing film, the refractive index change can be dominant optical signal. Especially, the polymeric film containing a dye that absorbs the light in the visible range can produce more improved refractive. Index changes as a result of sensing mechanism. The optimal analytical condition of high selectivity and sensitivity in the wider linear dynamic range was obtained metal ion-ligand interaction and effective detection of refractive index changes by the complexation of Cu^{2+} ion and squarylium dye in SPR measurement. Among 10 different alkali metals, alkaline earth metal and transition metal ions, squarylium dye in poly vinylchloride, poly vinyl acetate and poly vinyl alcohol copolymer film showed the highest selectivity to Cu^{2+} ion (Ock *et al.*, 2001).

Furthermore, additional sensitivity in the detection of Cu^{2+} ion by SPR was obtained by matching the wavelength of probing radiation of SPR and absorption maximum of squarylium-dye at 675 nm, which allow to detect small changes in the refractive index by complex formation on the sensing surface.

2.2.2 Use of squarylium dyes in optical data recording

Squarylium dyes are used in optical layers for optical data recording, using a laser with a wavelength up to 450 nm. In an invention made by Bayer and fleisch (1998), the invention relates to a write only read many (WORM) type optical data recording medium capable of recording and reproducing information with radiation of blue laser, which employs a squarylium based dye in the optical layer. The invention further relates to the use of the optical layer squarylium dyes write only read many (WORM) type optical recording medium, blue laser radiation capable of recording and reproducing information. Recently, organic dyes diode - laser optical storage areas

attracted considerable attention. Commercial recordable compact discs (CD-R), and recordable digital versatile discs (DVD-R) may contain recording layer based on phthalocyanine, hemicyanine, cyanine and metalized azo dyes (Sung *et al.*, 1998). These dyes are applicable to their respective fields of laser wavelength standard. Other general requirements for dye media are strong absorption, high reflectance, high recording sensitivity, low thermal conductivity, heat and light stability, non-toxicity of the storage durability. For industrial applications, these dyes must be suitable for the spin-coating method to prepare a film, that is, they must be sufficiently soluble in a spin coating method which is usually applied to the organic solvent. Recordable compact discs (CD-R) are well known WORM optical recording medium. Recently, a high increase in the information storage capacity of 4.7 Gigabytes digital versatile disc (DVD) has been commercialized. DVD-R technology uses a wavelength of 630-670 nm red diode laser as the light source. Pit size can be reduced and the tracks pitch, and compared with the case of CD-R, information storage capacity can be increased up to 6-8 times. Bayer *et al.*, (2003) disclosed squarylium dye as the information layer of the optical data carrier of the light absorbing compound.

2.2.3 Molecular sensor and bioimaging application of squarylium dye

The strong absorption and emission signal of squarylium chromophores are derived from charge transfer transitions, thus sensitive to the neighboring environment, e.g., solvent polarity, temperature, and other provocations. By evaluating the change of optical properties, the changes in environment can be monitored, which makes squarylium dyes good candidates as chemosensors. Using an indoleninium squarylium, Ioffe and Thompson (1969) successfully detected alterations in lipid bilayer membranes. Switching from water solution to a lipidic environment, the emission

intensity of the squarylium probe increased significantly along with a red shift. Moreover, the absorption and emission responses of the squarylium sensor in different liposome media were related to the bilayer polarity varied by addition of positively charged electrolyte cetyltrimethyl ammonium bromide (CTAB), anionic phospholipid cardiolipin (CL) and neutral sterol (Chol). This showed the applications of squarylium chromophores as a fluorescent probe for membrane related processes. Squarylium dyes applied for protein sensing and labeling are basically studied by model proteins such as bovine serum albumin (BSA), human serum albumin (HSA), ovalbumin, and avidin. Suzuki and Yokoyama (2007) used a very simple squarylium as a BSA protein sensor in (2007). Upon the addition of BSA, squarylium dye none covalently interacts with proteins, resulting in an observable colour change from orange to deep purple. Squarylium dye showed consistent concentration response to various proteins, which is promising compared with other commercially available protein detection materials. The author also found that after the formation of BSA complex, the stability to other non protein substances was also very good

2.2.4 Xerographic application of squarylium dyes

Xerography is dry copying process in which black or coloured powder adhere to part of a surface remain electrically charged after being exposed to light from an image of the document to be copied. Xerography is also known as electrophotography which is a printing and photocopying technique that works on the bases of electrostatic charges. The xerography process is the dominant method of reproducing images and printing computer data and is used in photocopier, laser printer and fax machine. Since the first finding of photoconductivity of squarylium dyes, they have been receiving much attention with respect to application in optoelectronic field such as Xerography and

photoenergy conversion. The intense light absorption and highly polarized D-A-D structure of squarylium dyes make them applicable to photo-driven electronic material based on generation of the electron-hole pair. The device is often fabricated using the squarylium dyes in the solid states. In addition to photoconducting property, the D-A-D intramolecular charge transfer of squarylium has been giving opportunity to develop low band-gap conductive material. Recent advancement of squarylium dyes in electronics and optoelectronic field has been investigated by Yagi and Hiroyuki (2002) for example, xerographic device, anilino-type squarylium dye has been applied as charge generation layer (the typical principle of xerography). Considering the light source used in the device, they are suitable because of large light absorption in the visible – to- near IR region (Sung *et al.* 1999). High photoconductivity of squarylium dyes as well as their large light absorptivity in the low energy region of the solar-illumination wavelength is suitable for developing solar cell device. Nowadays squarylium dyes are receiving increasing interest as sensitizers for TiO₂ electrode in Gratzel- type solar cells (Sung *et al.* 1999)

2.2.5 Biological application of squarylium dyes

For a few decade, organic functional dyes have been receiving increasing attention with respect to application as labelling and chemosensory materials, environmental and biological important analytes such as typical and transition metal, proteins, nucleic acid, carbohydrate, and so on. Obviously, the techniques of the labelling and sensing of chemical have been developing in parallel with the development of host-guest and super molecular chemistry. The analyte bind to the dye (or dye appended receptor) to bring about the change of electronic environment around the chromophore. Thus, the spectral changes of the light absorption and /or fluorescence emission occur to make possible

the detection of the analyte. Hence, non covalent interaction between the dye and the analyte lead to non-destructive detection. Squarylium dyes are suitable for such application because they exhibit intense light absorption from visible to near-IR region.

2.3 Fibre Structure in Relation to Dye Molecular Structure

Textile fibres, natural or synthetic are made up of polymer molecules as their basic units. The functional groups within the polymers retain their chemical properties and this determines the type of dyestuff for which the fibre will have affinity for.

Generally, fibres with many polar functional groups (hydrophilic fibre) will have better affinity for ionic dyestuffs and those with few polar groups or no polar groups (hydrophobic fibre) will have greater affinity for non-ionic dyestuff. Crystallinity tends to impart hydrophobicity to fibre even those having polar groups. This is due to the screening—off of polar functional groups with prevalent intermolecular hydrogen bonds. Also, close packing of polymer molecules leaves little or no space for dye molecule to penetrate (Peter and Ingamells, 1960).

2.4 Polyester

Polyester is a term often defined as “long-chain polymers chemically composed of at least 85% by weight of an ester and a dihydric alcohol and a terephthalic acid”. In other words, it means the linking of several esters within the fibres. The major polyester in common use is polyethylene terephthalate, an ester formed by the step growth polymerization of terephthalic acid and ethylene glycol.

Polyester is available in three main types

Disperse-dyeable, basic-dyeable and acid-dyeable

Modification opens up the structure of the standard fibre which lead to increased affinity for disperse dyes and if the portion of the terephthalic acids units in the chain is substituted by sulpho-isophthalics acid molecule the negative potential conferred by the sulphonic acid group gives to the fibre an affinity for basic dyes and affinity for acid dyes can be imparted by the incorporation of basic groups.

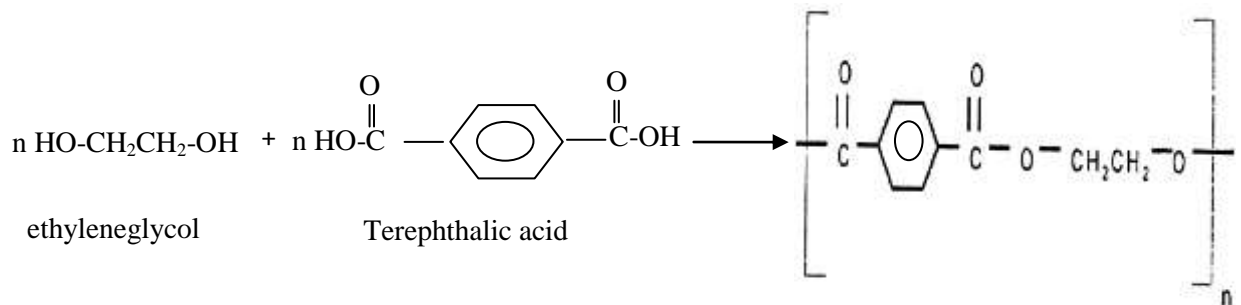


Figure 2.2: Synthesis of polyester

2.5 Properties of polyester

1. Polyester fabrics and fibres are extremely strong.
2. Polyester is very durable, resistant to most chemicals, stretching and shrinking, wrinkle resistant, and mildew and abrasion resistant.
3. Polyester is hydrophobic in nature and quick drying. It can be used for insulation by manufacturing hollow fibres.
4. Polyester retains its shape and hence is good for making outdoor clothing for harsh climates.
5. It is easily washed and dried.

Figure 2.3: Synthesis of nylon 6

2.8 Properties of Nylon 6

Nylon 6 fibres are tough, possessing high tensile strength, as well as elasticity and lustre. They are wrinkle-proof and highly resistant to abrasion and chemicals such as acids and alkalis. The fibres can absorb up to 2.4 % of water, although this lowers tensile strength. The glass transition temperature of nylon 6 is 47 °C.

2.9 Applications of Nylon 6

Nylon 6 finds application in a broad range of products requiring materials of high strength.

It is widely used for gears, fittings, and bearings, in automotive industry for under-the-hood parts, and as a material for power tools housings.

Nylon 6 is used as thread in bristles for toothbrushes, surgical sutures, and strings for acoustic and classical musical instruments, including guitars, sitars, violins, violas, and cellos.

It is also used in the manufacture of a large variety of threads, ropes, filaments, nets, and tire cords, as well as hosiery and knitted garments.

It can also be used in gun frames, which are made with a composite of nylon 6 and other polymers

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

Squaric acid 97% purity, 2-Amino-6-nitrobenzothiazole 97% purity, and 4-aminoacetophenone 98% purity, were purchased from Senya chemicals China. Other solvents and reagents were purchased from Nigeria. The materials used were acetone, ethanol, dichloromethane, DMF, toluene, 1-butanol, phenol, aniline, 3-aminophenol, 4-chloroaniline, 4-nitroaniline, 4-bromoaniline, p-anisidine, 4-aminobenzoic acid, N,N-dimethylaniline, N,N-diethylaniline, nitrobenzene, 4-aminoacetophenone, histidine-hydrochloride-mono-hydrate, disodium hydrogen-orthophosphate, hydrochloric acid, tetraoxosulphate-6-acids, sodium hydroxide, acetic acid, sodium dithionite, 100 % Polyester, and 100 % nylon 6 were purchased from samaru market Zaria. Solubility, burning and melting point test were carried out on the fabrics.

3.2 Apparatus and Equipment

50 ml conical flask, 50 ml beakers, 250 ml beaker, 250 ml 3-necked flask, 250 ml condenser, funnel, oven, electronic balance, filter paper, 50 ml flat-bottomed flask, sample bottles, spatula, test-tube boiling tube, wash-bottle, pH-meter, thermometer, Gallenkamp melting point apparatus, UV-visible spectrophotometer, FTIR SHIMADZU machine, GC-MS SHIMADZU machine and Reflux condenser.

3.3 Synthesis of Squaric Acid

- ❖ Squaric acid was synthesised by reacting hexachlorobutadiene (0.096 moles, 25 g) with excess morpholine (50 ml) and toluene (25 ml). The mixture was heated in an oil bath for 7 hours under reflux.

- ❖ It is then cooled, at 60 °C followed by addition of sodium acetate/acetic acid buffer (200 ml), and heated for 16 hours
- ❖ After cooling, 60 ml of sulfuric acid was added. The reaction was further reflux for 24 hours. followed by filtration and washing with 50 ml water and 50 ml acetone, and dried

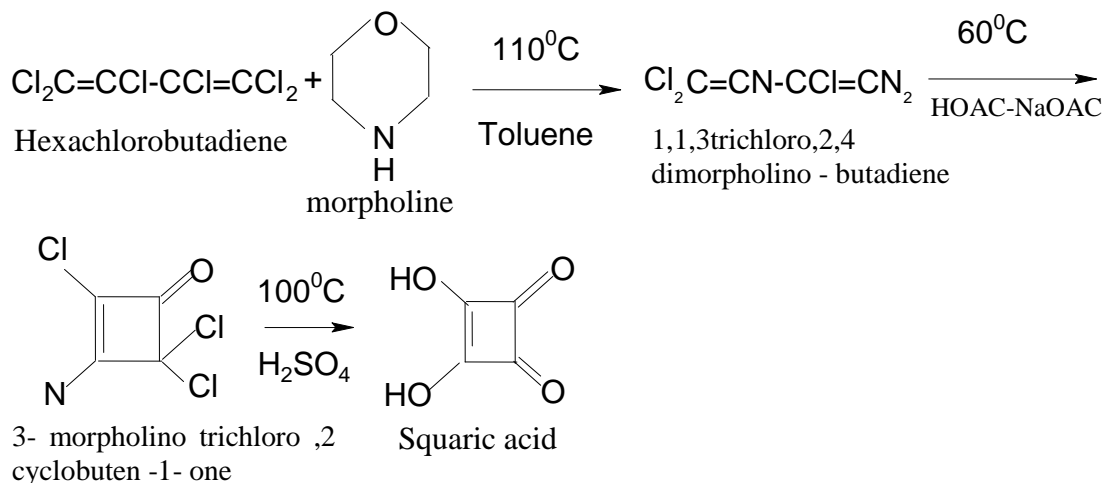


Figure 3.1 Reaction scheme for the synthesis of squaric acid

3.4 General Procedure for Synthesis of Squarylium Dyes

Squarylium dyes are prepared by condensation reaction of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) with arylamine.

About 0.290 g (0.0025 moles) of squaric acid was heated under reflux in a mixture of 1-butanol (40 mL) and toluene (20 mL). Then water was distilled off azeotropically using a Dean-Stark trap. After 1 hour, the appropriate (different substituted) primary aromatic amines 5 mmol (0.005 moles) was added and the reaction mixture refluxed for additional 4 hours. The suspension was cooled at room temperature and the solvent removed on a rotary evaporator. The residue was crystallized from 1-butanol and the solid obtained was dried in an oven at 50°C

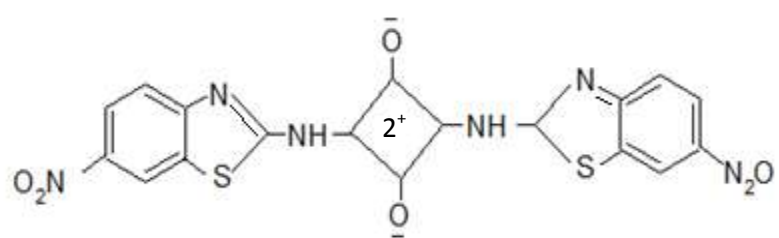
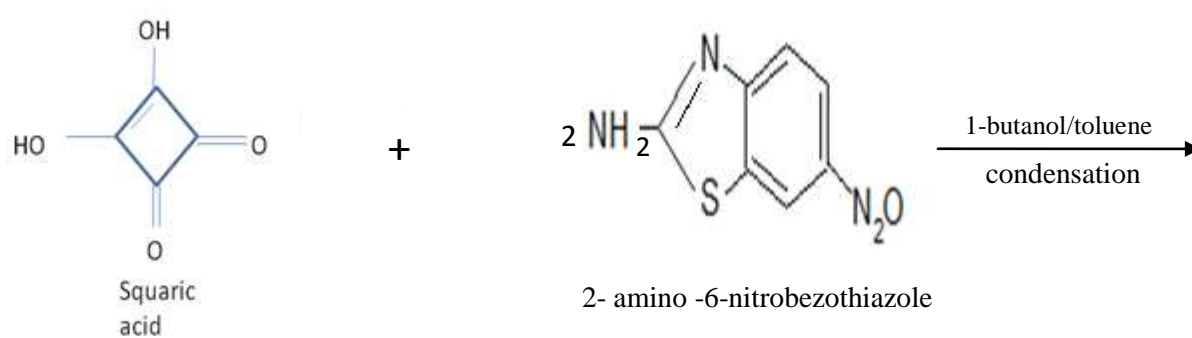


Figure 3.2: Squarylium dye synthesised from 2-amino-6-nitrobenzothiazole

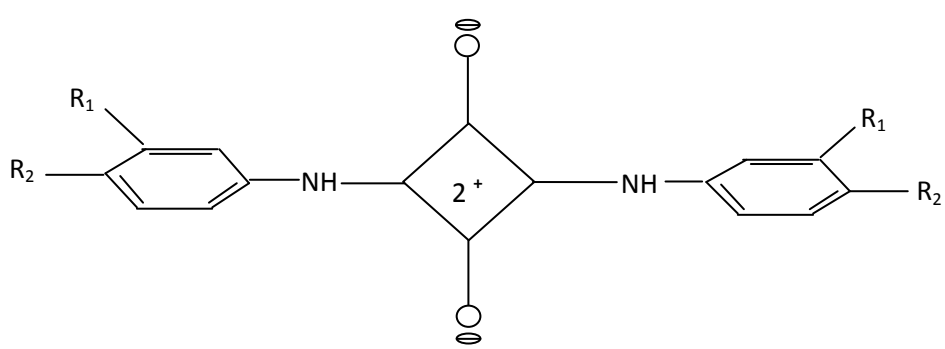
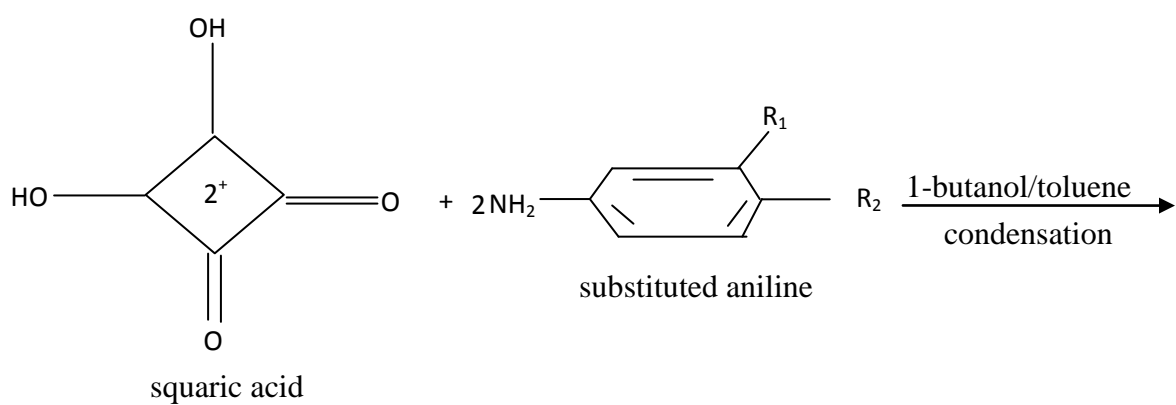


Figure 3.3: Reaction route for the synthesis of squarylium dyes

The same procedure used for dye A was used for all the other dyes, but different substituted Primary aromatic amines were used.

Where Dye B $R_1 = OH$ $R_2 = H$ Dye C $R_1 = H$ $R_2 = Br$ Dye D $R_1 = H$ $R_2 = Cl$ Dye

E $R_1 = H$ $R_2 = NO_2$ Dye F $R_1 = H$ $R_2 = H$ Dye G $R_1 = H$ $R_2 = COOH$

Dye H $R_1 = H$ $R_2 = OCH_3$ Dye I $R_1 = H$ $R_2 = C_2H_5O$

3.5.1 Synthesis of dye A

This was condensed with 2-amino-6-nitrobenzothiazole using the procedure above.

3.5.2 Synthesis of dye B

The procedure used was similar to that of dye A, except that 3-aminophenol was used as the condensing component.

3.5.3 Synthesis of dye C

The procedure used was similar to that of dye A, except that 4-bromoaniline was used as the condensing component.

3.5.4 Synthesis of dye D

The procedure used was similar to that of dye A, except that 4-chloroaniline was used as the condensing component.

3.5.5 Synthesis of dye E

The procedure used was similar to that of dye A, except that 4-nitroaniline was used as the condensing component.

3.5.6 Synthesis of dye F

The procedure used was similar to that of dye A, except that aniline was used as the condensing component.

3.5.7 Synthesis of dye G

The procedure used was similar to that of dye A, except that 4-aminobenzoic acid was used as the condensing component.

3.5.8 Synthesis of dye H

The procedure used was similar to that of dye A, except that p-anisidine acid was used as the condensing component.

3.5.9 Synthesis of dye I

The procedure used was similar to that of dye A, except that 4-aminoacetophenone was used as the condensing component.

3.6 Purification of Dyes

The synthesised dyes were purified by recrystallization method, using different solvents based on the principles of recrystallization i.e. solvents chosen were that in which the dyes were soluble at boil ,filtered and allow to cool for the crystals to appear, solvent used were nitrobenzene, and chloroform.

3.7 Determination of Melting Point of the Dyes

The melting point of the synthesised dyes was determined using the Gallenkamp melting point apparatus, (Department of Pharmaceutical Chemistry, ABU, Zaria).

3.8 Percentage yield of the Dyes

The percentage yield of the synthesised dyes was determined using the formula shown below:

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

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

3.9 Infra – Red Spectra of the Dyes

The infra-red spectra of each dye was determined using (Nicolet IR100) FT-IR spectrophotometer (NARICT, ZARIA) to determine the functional group present in each dye

3.10 UV- Visible Absorption Measurements

The wave length of maximum absorption of each dye (λ_{max}) was determined in three solvents. Dimethylformamide (DMF), ethanol and acetone. 0.01 g of each dye was dissolved in 5mls of each of the solvents. The spectrum of each dye solution was measured and recorded using UV-Visible spectra scanning machine at Pharmchem Department, ABU, Zaria.

3.11 Gas-Chromatography-Mass Spectroscopy (GC-MS) of the Synthesised Dyes

The structural elucidation of the synthesised dyes was determined using the GC/MS machine, (NARICT ZARIA).

3.12 Determination of Molar Extinction Coefficient

The molar extinction co-efficient (ϵ) was determined for each of the dye.

Beer-Lambert's law was applied in the determination of the molar extinction co-efficient using the following formulae:

$$\text{Log}_{10} \left(\frac{I_0}{I} \right) = \epsilon cl \dots \dots \dots (1)$$

$$A = \epsilon cl \dots \dots \dots (2)$$

$$\epsilon = A/cl \dots \dots \dots (3)$$

where:

$\text{Log}_{10} (I_0 / I)$ = absorbance (A) or optical density (OD)

I_0 = intensity of incident light

I = intensity of transmitted light

ϵ = molar extinction coefficient

A = absorbance or optical density

c = concentration of dye in moles/litre

l = cell path length (1cm)

The molar extinction coefficient were calculated based on the concentration of the dyes

3.13 Application of Dyes to Substrates

The dyes were applied to two substrates, 100 % Polyester and 100 % Nylon 6.the samples were confirm using solubility test, burning test and melting point.

3.13.1 Scouring

The samples were treated with 1 -2 % Na_2CO_3 solution for 15 minutes at the boil, with few drops of lux soap the samples were removed, rinsed thoroughly with water and dried.

3.13.2 Dyeing of polyester fabric

In the dyeing of polyester fabric carrier method of dyeing was used. The polyester fabrics were cut into 0.5 g size samples. Each sample was dyed in a dye bath made up of 10 ml of 1.25 g/l phenol, 20 ml of 17 g/l anionic detergent and 70 ml of water. The liquor ratio is 50:1. The depth of shade was 2 %. The fabric was wetted and thoroughly squeezed to remove excess water. It was immersed into the bath at 50°C and allowed to 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 substrates were removed, squeezed and rinsed thoroughly under running tap and allowed to dry at room temperature (Griffith and Rahman, 1992; Nkeonye, 1987; Micah and Ahmad, 2013).

3.13.3 Dyeing on nylon 6 fabric

1 % Stock solution of each dye was prepared, a liquor ratio 50:1 was used, 2 % shade on the weight of the fabric (OWF) and 0.5 g of Nylon 6 was used. The pH was varied from pH 2 to pH 12.

The volume required from each stock solution was calculated based on the formula

$$V = P \times \frac{w}{c}$$

where

P is the percentage shade

W is weight of fabric

C is the percentage concentration of solution. For the polyester fabric a carrier (phenol) and a dispersing agent were used to facilitate the dyeing process and the dyeing was carried out at 100⁰C

3.14.1 Effect of time on dyeing

The effect of time was determined for each dye, the dyeing time on dye exhaustion was determined for each dye by varying the time from 10 minutes to 1 hour at an interval of 25 minutes, with other conditions constant.

3.14.2 Effect of temperature on dyeing

The effect of temperature on dye exhaustion for each dye was observed by varying the temperature from 40⁰C to 100⁰C and keeping other conditions constant.

3.14.3 Effect of pH on dyeing

The effect of pH was studied on nylon 6 fabrics from pH 2 to pH 12 and keeping other conditions constant.

3.14.4 Effect of carrier concentration on dyeing

The effect of carrier concentration on dyeing was observed on polyester fabric from 0.25 g/l to 1.25 g/l and keeping other conditions constant.

3.14.5 Reduction clearing

The polyester dyed samples were treated in a bath containing 1 g/l dispersing agent, 2 g/l caustic soda and 2 g/l sodium dithionite at 60⁰C for 30 minutes. The aim was to remove unfixed dyes and carrier residues that may be left on the fabric after dyeing.

3.15 Determination of Dye Exhaustion

The absorbance of the dye-bath solution before dyeing for all the dyes were determined and absorbance of the dye-bath solution after dyeing for all the remaining dye liquors were also measured.

The exhaustion calculated in each case using the formula

$$\% \text{ Exhaustion} = \frac{(\text{OD}_1 - \text{OD}_2) \times 100 \%}{\text{OD}_1}$$

Where; OD₁ = optical density before dyeing

OD₂ = optical density after dyeing

3.16 Wash Fastness Test

The dyed samples were subjected to ISO 3 wash fastness test. The specimen was prepared by cutting the dyed sample into 10 cm × 4 cm dimensions. These samples were made into composites by stitching the test specimen made up of the dyed sample placed in between an un-dyed white cotton fabric and un-dyed fabric specimen of the same dimension 10 cm × 4 cm. The composite was agitated in a solution made up of 5 g/l soap solution and 2 g/l soda ash solution, using liquor ratio of 50:1. The washing was carried out at 60⁰C ± 2⁰C for 30 minutes. The composite was then separated and dried. The change in colour of samples and the staining of the adjacent un-dyed fabric

was assessed with appropriate grey scale (ISO 105-AO3:1987 5th Edition) (Nkeonye, 1987).

3.16.1 Assessment of Change in Colour

The change in colour of the test specimen is the change in depth or hue of the original dyed sample. The assessment is based on the degree of visual contrast between the original dyed material and tested material. Grey scale for assessing change in colour was used to determine the change of hue after the washing test, the degree of contrast between pair of colours in the standard grey scale for assessing change in colour was used in rating. The fastness rating of the specimen under test is the number of this grey scale contrast.

3.16.2 Assessment of Staining

The white cotton and the stained specimen were assessed using the same procedure for assessing change in colour but using the grey scale for assessing staining.

3.19 Perspiration Fastness Test

This procedure is a test for determining the fastness of the dyed fabrics to the effect of perspiration. Alkaline and acidic perspiration solutions were prepared.

3.19.1 Alkaline solution

5 g/l sodium chloride, (NaCl)

2.5 g/l disodium hydrogenorthosphate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$).

0.5 g/l histidine monohydrochloride-monohydrate ($\text{C}_6\text{H}_9\text{O}_2\text{N}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$).

The solution was brought to pH 8 using 0.1M NaOH

3.19.2 Acidic Solution

5 g/l sodium chloride, (NaCl)

2.2 g/l sodium hydrogen orthophosphate ($\text{NaHPO}_4 \cdot 2\text{H}_2\text{O}$).

0.5 g/l histidine monohydrochloride-monohydrate ($\text{C}_6\text{H}_9\text{O}_2\text{N}_3 \cdot \text{HCl} \cdot \text{H}_2\text{O}$).

The solution was brought to pH 5.5 using 0.1M acetic acid solution.

3.19.3 Procedure for perspiration test

The specimens were prepared as in washing fastness test. Then, the composite specimens were first wetted thoroughly and separately in the alkaline and acidic solutions respectively at room temperature for 30 minutes in a LR of 50:1. At the end of 30 minutes, the specimens were brought out of the perspiration solutions, squeezed slightly to remove excess liquor and are then separately placed between two glass plates each under a weight of 4.5 Kg. These treated composites are then placed in a perspirometer at $37 \pm 2^\circ\text{C}$ for 4 hours. At the end of 4 hours, the assembly is removed from the perspirometer and dried at room temperature (20°C).

3.20 Light Fastness Test

The tests were carried out on the dyed samples under daylight for nylon 6 and polyester. The procedures involved aligning both the eight blue wool standard together with a $5 \text{ cm} \times 2 \text{ cm}$ cut pieces of the dyed samples on a card and covering on third of the setup with opaque cover. Exposure was carried with regular inspection noting when the non-exposed part and the exposed part of each dyed sample had contrast equivalent to grade 4 ISO grey scales after which an opaque cover was placed covering part of the exposed sample part exposure was continued till the standard 3 faded. The rating of the dyed samples was taken to be those equivalent to that of standard dyed blue wool samples, which faded to the same extent as the specimen at the same time.

3.21 Determination of Fastness to hot Pressing

Fastness to pressing was carried out under three different conditions, dry, damp and wet (Saville, 2002).

3.21.1 Dry

The specimen was placed on dry un-dyed cotton adjacent fabric and pressed for 15 seconds with a heated press (a domestic iron was used, polyester: 120-150°C. nylon 6: 100-120°C).

It was then assessed immediately and after 4 hours interval for colour change and the adjacent for staining

3.21.2 Damp

The dry specimen was placed on dry cotton adjacent fabric, covered with wet cotton adjacent fabric and pressed for 15 seconds. It was then assessed as before.

3.21.3 Wet

The specimen was wetted and placed on dry cotton adjacent fabric and then covered with wet cotton adjacent fabric and pressed for 15 seconds. It was then assessed as before.

CHAPTER FOUR

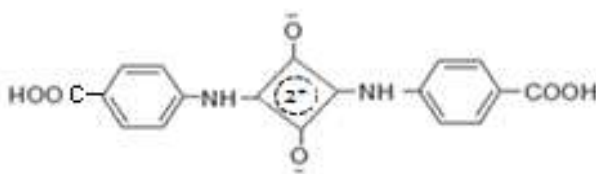
4.0 RESULTS

4.1 Synthesised squaric acid and squarylium Dyes

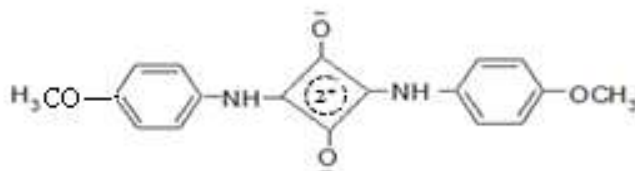
Table 4.1: Structures of the Synthesised Dyes

Dye sample	Dye Structure
A Prepared from 2-amino-6-nitrobenzothiazole	
B Prepared from 3-aminophenol	
C Prepared from 4-bromoaniline	
D Prepared from 4-chloroaniline	
E Prepared from 4-nitroaniline	
F Prepared from aniline	

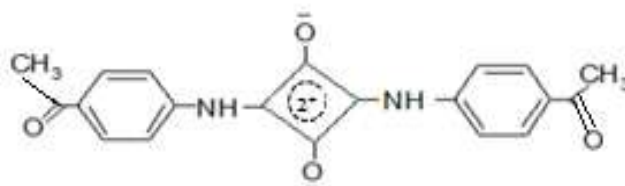
G Prepared from 4-aminobenzoic acid



H Prepared from 4-methoxyaniline



I Prepared from 4-aminoacetophenone



4.2 Physical Properties of the Synthesised Dyes

The molar extinction coefficient, molar mass, melting point, molar mass and the percentage yield of the synthesised dyes are shown in Table 4.2

Table 4.2: Physical properties of the synthesised dyes

Dye	Molar mass (g/mol)	Colour	Melting point (°C)	Percentage yield (%)	Molar extinction coefficient (Lmol⁻¹cm⁻¹ x 10⁵)
A	468	Red	318 – 320	97	6.1700
B	296	Yellow	300 – 301	53	6.8087
C	422	Yellow	310 – 311	78	8.4400
D	333	Yellow	270 – 272	69	6.6600
E	354	Yellow	300 – 301	90	7.7882
F	264	Yellow	302 – 305	97	5.2812
G	352	Yellow	322 – 325	82	8.8028
H	324	Yellow	332 – 336	87	7.2045
I	348	Yellow	270 – 280	91	9.3962

The analysis of the visible absorption of the synthesised dyes is shown in Table 4.3.

Table 4.3: Visible absorption spectra of synthesised dyes

Dye	λ_{max} DMF (nm)	λ_{max} Ethanol (nm)	λ_{max} Acetone (nm)
A	500	442	414
B	460	420	419
C	438	415	413
D	440	411	407
E	458	410	406
F	437	412	404
G	448	409	403
H	435	408	402
I	442	407	400

4.4 Infra-Red Spectra of the Synthesised Dyes

Table 4.4: Analysis of the infra-red spectra of the synthesised dyes

Dye	N – H	C- C	OH		C-H	C = C	N-O	C-Cl	OCH ₃	C=O
	Str		Str	Ben	Ben	Str	Str	Str	Str	Str
A	3406.4	1426.4			826.5	2353.2	1642.2	1332.8		
B	3411.2	1459.2	3753.6	1396.5	879.5	2945.4	1566.2			
C	3460.2	1417.7			825.5	2956.9	1594.2			
D	3474.8	1413.8			825.5	2956.9	1594.2	673.1		
E	3432.4	1421.5			802.4	2959.8	1586.5	1339.6		
F	3411.2	1417.7			821.7	2946.3	1591.3			
G	3072.2	1587.4	3407.3	1403.2	834.2	2968.5	1587.4			1681.9
H	3404.0	1424.6			824.6	2952.1	1593.0		2367.7	
I	3431.5	1415.8			825.5	2969.5	1603.8			

Table 4.5: Mass spectra of the synthesised dyes (m/z)

Dye	Fragment	Experimental	Calculated
A	CNO^+ , C_2HNO^+ , $\text{C}_3\text{H}_3\text{NO}^+$, $\text{C}_3\text{H}_8\text{NO}^+$, $\text{C}_3\text{H}_7\text{N}_2\text{O}^+$, $\text{C}_4\text{H}_6\text{N}_2\text{O}^+$, $\text{C}_5\text{H}_4\text{SNO}^+$, $\text{C}_7\text{H}_5\text{SO}^+$, $\text{C}_7\text{H}_5\text{NSO}^+$, $\text{C}_8\text{H}_8\text{N}_3\text{SO}^+$	194	194
B	C_2H_3^+ , C_3H_5^+ , C_3H_7^+ , $\text{C}_3\text{H}_5\text{O}^+$, C_5N^+ , $\text{C}_6\text{H}_8\text{N}^+$, C_9H_7^+ , $\text{C}_{10}\text{H}_9^+$ $\text{C}_9\text{H}_6\text{NO}^+$, $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_2^+$, $\text{C}_{11}\text{H}_7\text{N}_2\text{O}_2^+$, $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4^+$	298	296
F	C_2H_3^+ , C_3H_5^+ , C_4H_7^+ , C_5H_9^+ , C_6H_2^+ , C_6HN^+ , $\text{C}_6\text{H}_{12}\text{N}^+$, C_9HN^+ , C_9NO^+ , $\text{C}_{10}\text{N}_2\text{O}_2^+$, $\text{C}_{13}\text{H}_6\text{N}_2\text{O}_2^+$, $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2^+$.	264	264
H	C_2H_3^+ , C_3H_5^+ , C_3H_7^+ , $\text{C}_3\text{H}_5\text{O}^+$, C_6H_2^+ , C_7H_3^+ , C_8H_5^+ , C_9H_6^+ , $\text{C}_9\text{H}_6\text{N}^+$, $\text{C}_{10}\text{H}_3\text{N}^+$, C_{13}NO^+ , C_{14}NO^+ , $\text{C}_{14}\text{N}_2\text{O}_2^+$, $\text{C}_{15}\text{N}_2\text{O}_2^+$, $\text{C}_{20}\text{N}_2\text{O}^+$, $\text{C}_{20}\text{H}_{10}\text{N}_2\text{O}_3^+$.	326	324

Table 4.6: Dye Exhaustion on nylon 6 and polyester fabrics

Dye	% Exhaustion on nylon 6	% Exhaustion on polyester
A	92	68
B	80	78
C	35	30
D	38	32
E	84	77
F	86	85
G	70	57
H	33	30
I	82	80

4.5 Dye Application

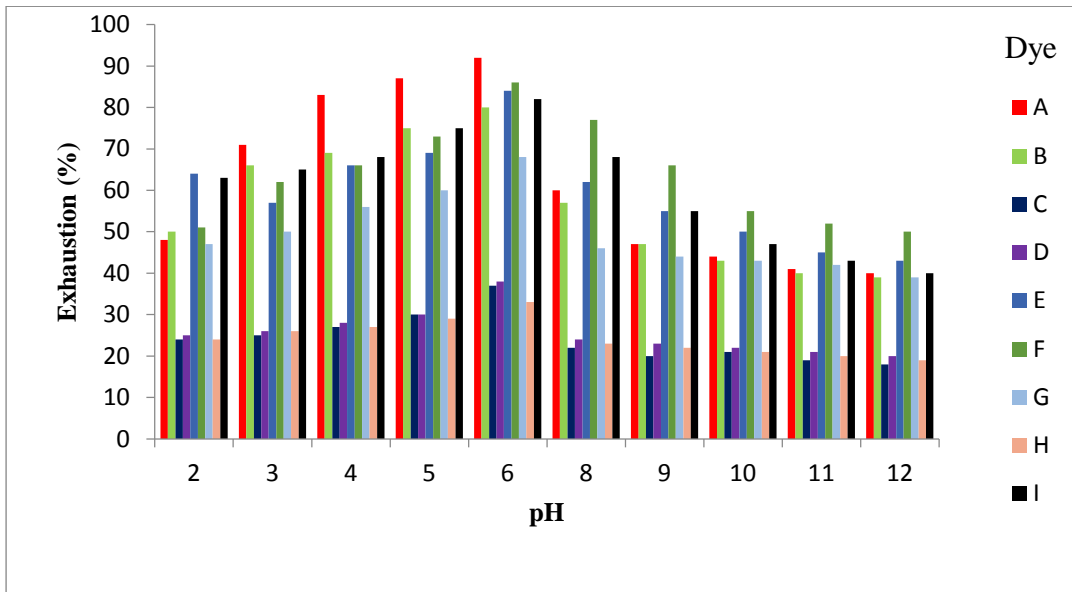


Figure 4.6.1: Effect of dye bath pH on % exhaustion on nylon 6 using dyes A-I

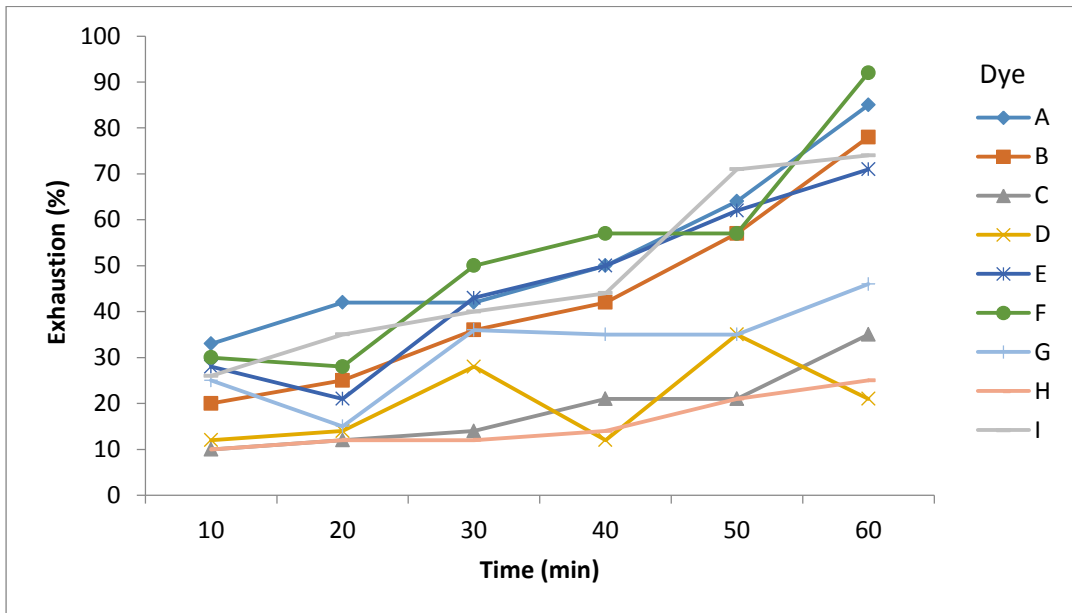


Figure 4.6.2: Effect of dyeing time on % exhaustion on nylon 6 using dyes A-I

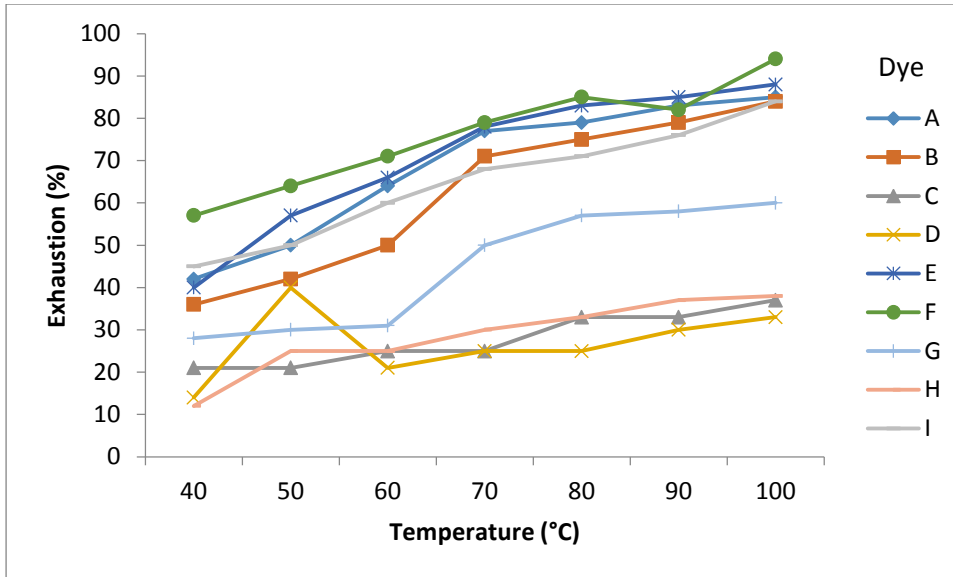


Figure 4.6.3: Effect of temperature on % exhaustion on nylon 6 using dyes A-I

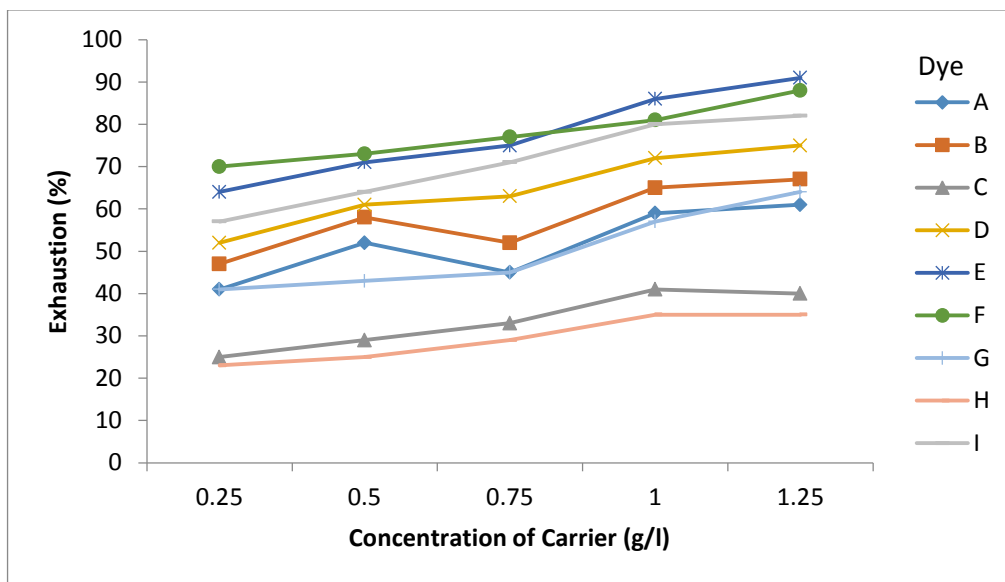


Figure 4.6.4: Effect of carrier concentration on % exhaustion on polyester using dyes A-

I

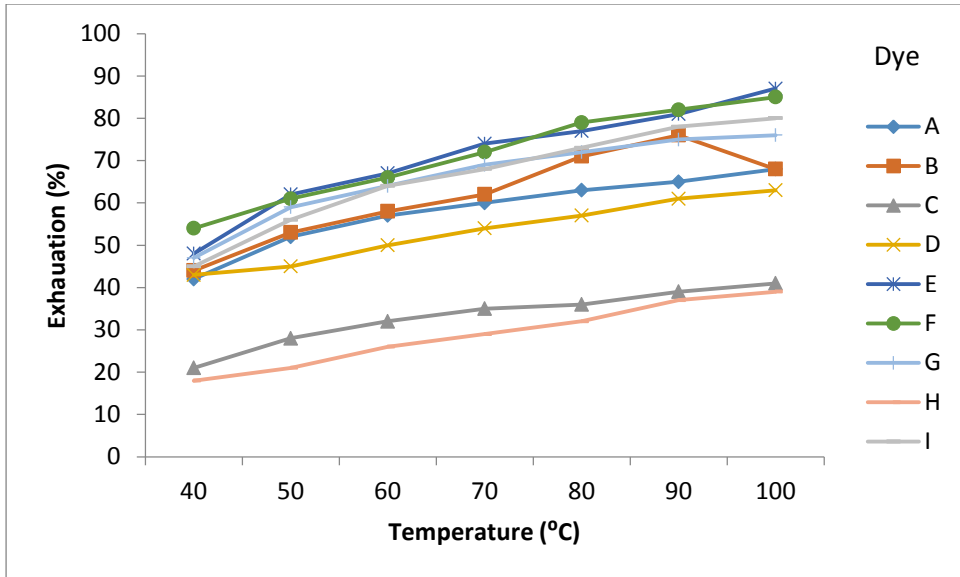


Figure 4.6.5: Effect of temperature on % exhaustion on polyester using dyes A-I

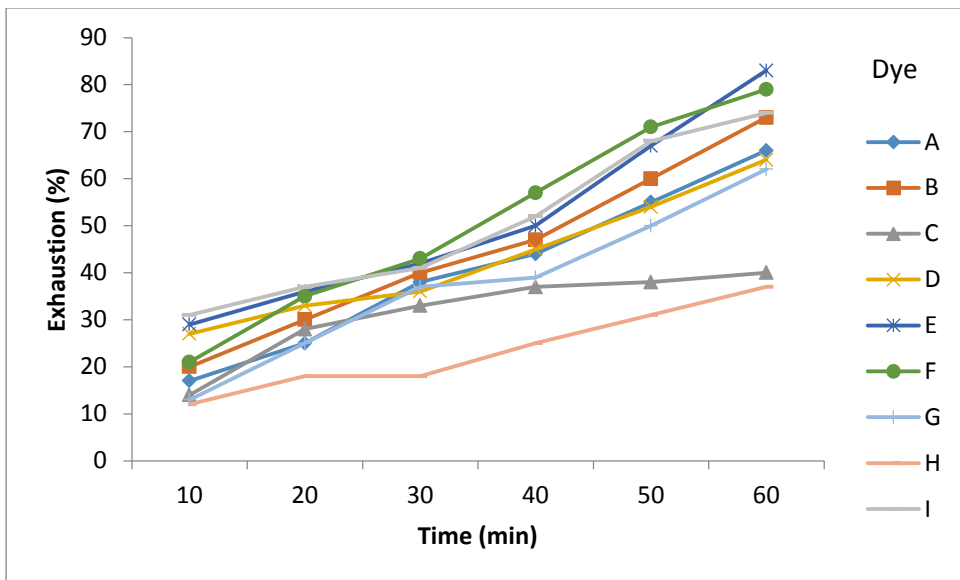


Figure: 4.6. 6: Effect of time on % exhaustion on polyester using dyes A-I

4.6 Wash Fastness

Table 4.6.1: Wash fastness of dyes A-I on nylon 6 using ISO 3 standard

Samples		Wash fastness	
Dyed nylon 6 fabrics	Change in colour	Staining on cotton	
A	4	4	
B	4	4	
C	2	2	
D	2	2	
E	4	4	
F	4	4	
G	4	4	
H	2	2	
I	4	4	

Table 4.6.2. Wash fastness of dyes A-I on polyester using ISO 3 standard

Samples	Wash fastness	
	Change in colour	Staining on cotton
Dyed polyester fabrics		
A	5	5
B	5	5
C	3	3
D	3	3
E	5	5
F	5	5
G	5	5
H	3	3
I	5	5

Table 4.6.3: Light fastness of dyes A-I on nylon 6 and polyester

Dyed samples	Rating on Nylon 6	Rating on Polyester
A	6	5
B	6	5
C	4	3
D	4	3
E	6	5
F	6	5
G	5	5
H	4	3
I	6	5

Table 4.6.4: Fastness to hot pressing of dyes A-I on polyester

Samples	Wet		Dry		Damp	
Polyester	Colour change	Staining on cotton	Colour change	Staining on cotton	Colour change	Staining on cotton
A	4	4	4	4	4	4
B	5	4	5	5	5	4
C	3	3	3	3	3	3
D	3	3	3	3	3	3
E	5	5	5	5	5	5
F	4	4	5	5	5	5
G	4	4	4	4	4	4
H	3	3	3	3	3	3
I	5	5	5	5	5	5

Table 4.6.5: Fastness to hot pressing of dyes A-I on nylon 6

Sample	Wet		Damp		Dry	
Nylon 6	Colour change	Staining on cotton	Colour change	Staining on cotton	Colour change	Staining on cotton
A	4	4	5	5	5	5
B	4	4	5	5	5	5
C	3	3	3	3	3	3
D	3	3	3	3	3	3
E	5	5	5	5	5	5
F	4	4	5	5	5	5
G	4	4	4	4	4	4
H	3	3	3	3	3	3
I	5	5	5	5	5	5

Table 4.6.6: Fastness to perspiration of dyes A-I on polyester

Polyester	Acidic Condition		Alkaline Condition	
Dye	Colour change	Staining on cotton	Colour change	Staining on cotton
A	4	4	4	4
B	5	5	4	4
C	3	3	3	3
D	3	3	3	3
E	5	5	5	5
F	5	5	4	4
G	4	4	4	4
H	3	3	3	3
I	5	5	5	5

Table 4.6.7: Fastness to perspiration of dyes A-I on nylon 6 fabric

Nylon 6	Acidic Condition		Alkaline Condition	
Dye	Colour change	Staining on cotton	Colour change	Staining on cotton
A	5	5	5	5
B	5	5	4	4
C	3	3	3	3
D	3	3	3	3
E	4	4	5	5
F	5	5	4	4
G	4	3	4	3
H	3	3	3	3
I	5	5	5	5

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physical Characteristics of the Synthesised Dye

The physical characteristics of the synthesised dyes were shown in Table 4.2. Each of the different dyes synthesised possessed distinctive physical characteristics. The dyes exhibited well defined melting points. This generally shows that the values were quite high and ranged between 270 – 336⁰C which correspond with other literature values i.e. squarylium dyes possess high melting points (Yuanwei, 2008). The difference in their melting point could be due to the difference in molecular structure of the dyes. The dye condensed with p-anisidine gave the highest melting point of 332 – 336⁰C. The colour of the dye crystals varied from yellow to red for all the dyes. However, dye A condensed with 2-amino-6-nitrobenzothiazole gave a red colour while others condensed with 3-aminophenol, 4-bromoaniline, 4-chloroaniline, 4-nitroaniline, aniline, 4-aminobenzoic acid and 4-aminoacetophenone gave yellow colours. The yields ranged from 53-97 %.

5.2 Infra-red analysis of the synthesised dyes

The basis of infra-red analysis was to ensure that vital functional groups that identify the dyes were present. As seen from the infra red spectra result (Table 4.4 and Figures 4.4.1 – 4.4.9), the dyes gave absorption peaks due to primary aromatic amine (N-H) stretching vibration at 3400 – 3500 cm⁻¹, dye A gave N-O stretching vibration at 1350 ± 30, C = C stretching at 1600 – 1500 cm⁻¹, aromatic C – C stretching vibration band at 1457 - 1414 cm⁻¹, C – H aromatic bending vibration at 690 – 900 cm⁻¹. Dye B gave O-H stretching vibration at 3580 – 3650 cm⁻¹ and bending vibration at 1330 - 1430 cm⁻¹, C – C stretching vibration band at 1457-1414 cm⁻¹, C – H aromatic bending vibration at 690 – 900 cm⁻¹. C = C stretching vibration at 1600 – 1500 cm⁻¹. The same for dyes C

and F. dye D give C – Cl stretching vibration band at 679 cm^{-1} , dye E gave N-O stretching vibration at 1350 ± 30 , dye G gave C = O stretching vibration at $1637\text{--}1601\text{ cm}^{-1}$, O-H stretching vibration at $3589\text{--}3650\text{ cm}^{-1}$. OCH₃ stretching vibration band for dye H occurred at $2850\text{--}3000\text{ cm}^{-1}$, C = C stretching at $1600\text{--}1500\text{ cm}^{-1}$, aromatic C – C stretching vibration band at $1457\text{--}1414\text{ cm}^{-1}$, C – H aromatic bending vibration at $690\text{--}900\text{ cm}^{-1}$.

5.3 Mass Spectroscopy of the Synthesised Dyes

The elucidated structural information of the synthesised dyes were shown in Table 4.5 and Figures 4.5.1 – 4.5.4. The identified mass spectra of dye A shows fragment with mass - to - charge (m/z) ratio of 42, 55, 69, 74, 87, 98, 126, 137, 151 and parent 194 representing M⁺ and the corresponding positive charge fragment of CNO⁺, C₂HNO⁺, C₃H₃NO⁺, C₃H₈NO⁺, C₃H₇N₂O⁺, C₄H₆N₂O⁺, C₅H₄SNO⁺, C₇H₅SO⁺, C₇H₅NSO⁺, C₈H₈N₃SO⁺ was found. There was no difference between the calculated and the experimental, i.e. 194 g/mol.

The mass spectral of dye B also gave mass – to – charge ratio (m/z) of 27, 41, 43, 57, 74, 94, 115, 129, 144, 186, 198 and parent 298 representing M⁺ and the corresponding positive charge fragments of C₂H₃⁺, C₃H₅⁺, C₃H₇⁺, C₃H₅O⁺, C₅N⁺, C₆H₈N⁺, C₉H₇⁺, C₁₀H₉⁺, C₉H₆NO⁺, C₁₀H₆N₂O₂⁺, C₁₁H₇N₂O₂⁺, C₁₆H₁₂N₂O₄⁺. The difference between the experimental (298 g/mol) and the calculated value (296 g/mol), may be due to isotropy.

Dye F give a mass spectra of mass – to – charge ratio (m/z) of 27, 41, 55, 69, 74, 87, 98, 123, 138, 180, 222 and parent 264 representing M⁺ and the corresponding positive charge fragments C₂H₃⁺, C₃H₅⁺, C₄H₇⁺, C₅H₉⁺, C₆H₂⁺, C₆HN⁺, C₆H₁₂N⁺, C₉HN⁺, C₉N⁺, C₁₀N₂O₂⁺, C₁₃H₆N₂O₂⁺, C₁₆H₁₂N₂O₂⁺. There was no difference between the experimental (264 g/mol) and the calculated. Dye H gave a mass spectral of mass-to-

charge ratio (m/z) of 27, 41, 43, 57, 74, 87, 101, 114, 128, 143, 186, 198, 221, 240, 284, 293 and parent 326 representing M^+ and the positive charge fragment of $C_2H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_3H_5O^+$, $C_6H_2^+$, $C_7H_3^+$, $C_8H_5^+$, $C_9H_5^+$, $C_9H_6N^+$, $C_{10}H_3N^+$, $C_{13}NO^+$, $C_{14}NO^+$, $C_{14}N_2O_2^+$, $C_{15}N_2O_2^+$, $C_{20}N_2O^+$ and $C_{20}H_{10}N_2O_3^+$. The difference between the experimental (326 g/mol) and the calculated (324 g/mol) may be due to isotropy.

5.4 Solvatochromism

Solvatochromism is the effect of solvent polarity on the absorption spectra of dyes. Solvatochromism is due to various solute – solvent interactions in both the ground and excited states. The solvents used in this research as summarized in Table 4.3, are in the order of decreasing polarity of DMF, ethanol and acetone. The solvents were chosen because they have a wide difference in polarity. The results obtained reveal that, there is a general bathochromic shift with increasing solvent polarity. The wave-length of maximum absorption was highest in DMF and the least is acetone. Dye A for example absorbs at 414 nm in acetone, 442 nm in ethanol and 499 nm in DMF. dye B with 419 nm in acetone, 420 nm in ethanol and 460 nm in DMF, dye C 413 nm in acetone, 415 nm in ethanol and 438 nm in DMF, dye D 407 nm in acetone, 411 nm in ethanol and 440 nm in DMF, dye E absorbs at 406 nm in acetone, 410 nm in ethanol, and 458 nm in DMF. Dye F 404 nm in acetone, 412 nm in ethanol and 437 nm in DMF, dye G 402 nm in acetone, 409 nm in ethanol and 448 nm in DMF, Dye H 407 nm in ethanol and 448 nm in DMF, Dye H 401 nm in acetone, 408 nm in ethanol and 435 nm in DMF. Dye I absorbs at 400 nm in acetone, nm in ethanol and 442 nm in DMF. Generally the synthesised dyes exhibit positive solvatochromism. The bathochromic effect observed on changing to a more polar solvent such as DMF suggest that the dye molecules have a more polar excited state than the ground state, and a polar solvent was able to stabilized

this effect more at the ground state, thus lowering the transition energy (Venkataraman, 1970) with increasing polarity of solvent the absorption maximum is shifted to longer wavelength (Marini *et al.*, 2010). The energy difference between the ground and the excited states is reduced, leading to a bathochromic shift in the visible absorption band.

5.5 Molar Extinction Coefficient (ϵ)

The larger the molar absorptivity, the more probable the electronic transition. The molar extinction coefficient of the synthesised dyes was calculated based on the concentration of the dyes in DMF as solvent. The result obtained is shown in Table 4.2. From the Result, it can be seen that the dyes possess high molar extinction coefficient and this may be attributed to the fact that it transmits more light. From the result shown, it can be deduced that majority of the synthesised dyes gave molar extinction coefficient values greater than $5.2812 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. The higher molar extinction coefficient values of the synthesised dyes implies the probability for more electronic transition.

5.6 Dye Exhaustion for nylon 6 and polyester

From the results summarized in Table 4.6 dyes A, B, E, F, G and I applied to nylon 6 has percentage exhaustion of 92 %, 80 %, 84 %, 86 %, 76 % and 82 %, respectively. Also from the same Table 4.6 with respect to dye exhaustion on polyester it shows that dyes A, B, E, F, G and I have Percentage exhaustion of 68 %, 78 %, 87 %, 85 %, 55 % and 80 %, respectively. From the results obtained it is clear that the percentage exhaustion of both nylon 6 and polyester are quite different. However nylon 6 has relatively the highest Percentage exhaustion. Comparing dyes A with percentage exhaustion of 92 % dye B 80 % and dye I 82 % on nylon 6 with the result obtained from polyester with the same dyes A, B and I which gave the percentage dye exhaustion of

60 %, 78 % and 80 %. It can be seen that nylon 6 gave better percentage exhaustion of 92 % with A and 68 % exhaustion on polyester, with the same dye. It can be concluded from the result obtained that the synthesised dyes are better on nylon 6 than polyester fabric. This may be attributed to the amorphous nature of nylon 6 when compared with polyester. Also polyester been highly crystalline than nylon 6 which could reduce affinity. Crystallinity also tends to impart hydrophobicity to the fibre even those having polar groups. Nylon 6 is semi- crystalline fibre with amorphous regions for dye molecule to penetrate. However effective dye sites are screened off from the dye molecules in crystalline region (Trotman, 1975). Also, the close packing of polymer molecules leaves little or no space for dye molecules to penetrate (Peter and Ingamells, 1960). Very low percentage dye exhaustion was achieved on both nylon 6 and polyester with dyes C, D and H, this may be attributed to the presence in the structure of the dyes electron withdrawing groups such as Cl, Br, and OCH₃. In dyes C, D and H, respectively. The electron withdrawing groups tend to make the dye structure to be unstable by electron withdrawing. Nylon 6 and polyester been hydrophobic requires a low molecular weight dyes. Comparing dye A which is a heterocyclic group from 2-amino-6-nitrobenzothiazole is more stable than dyes C, D and H from benzene ring. Although dye H contains oxygen in the structure, but OCH₃ been more effective withdraws electrons from the dye structure thereby making the dye structure to be unstable. Hence the presence of Cl, Br and OCH₃ groups makes the heterocyclic ring electron deficient by electron withdrawing (Cohen and Coworker, 1959)

5.7 Effect of pH

The effect of pH on nylon 6 was carried out, for each 0.5 g fabric sample, the same dye concentration was prepared, 2 % shade, time of dyeing 1 hr at 100⁰C. But pH of dye-bath was varied as follows pH 2, pH 3, pH 4, pH 5, pH 6, pH 8, pH 9, pH 10, pH 11 and pH 12, respectively. It was generally observed that as pH of dye-bath was increased, exhaustion also increase in the acidic medium from pH 3, pH 4, pH 5, and pH 6. Dye uptake was observed to be best for nylon 6 at pH 6. For dyes A, B, E, F and I giving exhaustion of 92 %, 80 %, 84 %, 86 % and 82 %, respectively. In alkaline medium it was observed that the exhaustion was decrease as the pH was increased to pH 12, giving percentage exhaustion of 57 %, 62 %, 55 %, 68 % and 73 % respectively. The low dye exhaustion observed in the alkaline medium may be due to hydrolysis, because further increase in pH lowered the colour strength due to hydrolysis (Ahmad, 2012). It can be deduced that pH 6 is the best pH for dyeing nylon 6 fabric.

5.8 Effect of Time

From the result obtained in Table 4.8 in the appendix also graphically represented in figures 4.2 – 4.6, it was observed that as the time of dyeing increased the percentage exhaustion also increase for both nylon 6 and polyester fabrics, exhaustion was low at shorter time of dyeing this may be attributed to the assumption that at shorter time of dyeing, exhaustion is fairly achieved but as the time increase more dyes diffuse into the fibre. With time the molecules of the dye are transferred from solution to the surface of the fabric and adsorbed dye diffused mono molecularly into the fabric to form solid solution. This observation may be attributed to the molecular size of the dyes as well as rate of diffusion of the dye (Bello *et al.*, 2016).

5.9 Effect of Carrier Concentration

The squarylium dyes were applied to polyester, the result obtained are for the effect of varying carrier concentrations keeping other condition constant and are given in Table 4.9 and represented graphically in figure 4.4 Carrier concentrations were varied from 0.25 – 1.25 g/L. It was generally observed that as carrier concentration increase, dye exhaustion also increase. The highest exhaustion were obtained at carrier concentration of 1.25 g/L with dyes A, B, C, E, F, G and I giving exhausting of 61 %, 67 % 75 %, 91 %, 88 %, 64 % and 82 % respectively at 1 g/L the exhaustion obtained using the same dyes were 59 %, 65 %, 72 %, 82 % 81 %, 57 % and 80 % , respectively. It can be deduced that from the result obtained carrier concentration of 1.25g /L gave the best dye exhaustion. The least exhaustions were obtained at the lowest carrier concentration 0.25 g/L, i.e. 41 %, 47 %, 25 %, 52 %, 64 %, 70 %, 41 %, 23 % and 57 %. Polyesters are highly hydrophobic with a very compact structure and are highly crystalline (Vickerstaf, 1954) and posses high glass transition temperature (70 – 80°C) therefore, phenol as carrier, to enhance the dye penetration of the synthesised dyes with polyester, carriers function by facilitating dye diffusion, opening the fibre pores and increasing segments mobility of polyester fibre. Hence, at higher carrier concentration, dye exhaustion is also higher.

5.10 Effect of Temperature

It is thought that the higher the temperature of the dye bath, the greater the kinetic energy of the dye molecules and faster diffusion of the dye molecules in and out of the substrate. Since diffusion is directly proportional to the thermodynamic temperature (Bello *et al.*, 2016). The result obtained from the study of the effect of varying temperature on percentage exhaustion is shown in Table 4.10 and represented

graphically in figures 4.3 – 4.5. The temperature was varied from 40 to 100°C for both nylon 6 and polyester, it was generally observed that as the temperature of the dye bath was increased, migration improved, adequate leveling and penetration also occurred, thereby increasing the percentage exhaustion. dye uptake was observed to be best on nylon 6 at 100°C for dye A, B, E, F, G and I with other factors kept constant, giving exhaustion of 85 %, 84 %, 88 %, 94 %, 60 % and 87 % respectively.

On polyester using the same dyes the exhaustion obtained were 68 %, 78 %, 87 %, 85 %, 76 % and 80 % on dyes A, B, E, F, G, and I respectively. It was also observed that dye uptake was also best at 100°C for polyester. At 40°C the exhaustion was found to be 42 %, 45 %, 57 %, and 48 % for dyes A, E, F and I respectively. It can be seen that exhaustion was low at 40°C for nylon 6, when compared to polyester at 40°C. The exhaustion were 40 %, 42 %, 52 %, 46 % and 45 % for dyes A, B, E, F, G, and I on polyester fabric, high percentage exhaustion was obtained on nylon 6, at 40°C low percentage exhaustion was observed. Temperature in general increase the rate of any chemical reaction, the same thing occurs with dye but also with the water that the dye is dissolved in. Temperature affects the rate of dye exhaustion since diffusion is directly proportional of the thermodynamic temperature, the higher the temperature of the dye bath the greater the kinetic energy of the dye molecules and the faster the diffusion of that dye molecule in and out of the substrate. Increase in temperature also tends to increase the porosity by increasing the molecular entropy and amorphous region of fabric polymer matrix, a rise in temperature increases exhaustion rather than diminish; the exhaustion was greater at high temperature. It was observed that the highest absorbance was obtained at 100°C for both the nylon 6 and polyester fibres. At low temperature, the absorption is lower because the dye was not in the fibre, but only in the water when it gets hot.

5.11 Wash Fastness

The results were summarized in Tables 4.6.1 and 4.6.2. It was clearly shown that almost all the synthesised dyes gave a very good wash fastness on both nylon 6 and polyester dyed fabrics. All of the dyes on nylon 6 gave fastness rating of 4 for change in colour and 4 for staining of adjacent fabric, while polyester gave a fastness rating of 5 and 5 for staining of adjacent fabric. The dyes tend to have better wash fastness on polyester when compared to nylon 6. The wash fastness on nylon 6 was good while that of polyester was very good. The wash fastness property on nylon 6 and polyester dyed fabrics were generally good to very good. The very good fastness property on polyester dyed fabrics may be attributed to the crystalline nature of polyester. Which makes it difficult for the dye to diffuse into the fibre, and once in, it is difficult for the dye molecules to diffuse out thereby giving dyeing of high fastness to washing. Also, the good to very good wash fastness observed on both nylon 6 and polyester on dyes A, B, E, F, G and I, may be attributed to the nature of bond (hydrogen bond) that bind the dye and the substrates. Also presence of substituent such as NO_2 in dyes A and E, OH in dye B, NH_2 in dye F, COOH in dye G, and $\text{C} = \text{O}$ in I.

5.12 Light Fastness

The results of light fastness are summarized in Table 4.6.3. It was observed that the light fastness of the nylon 6 dyed fabrics were higher compared with the polyester dyed fabrics. The dyed nylon 6 fabric gave a fastness rating of 6 i.e. very good light fastness, while that of polyester gave rating of 5 i.e. good, this may be attributed to the effect of the carrier applied to polyester during dyeing which tend to reduce the light fastness on polyester, on the other hand the good light fastness of nylon 6 may be attributed to the molecular structure of the dye, and dye substituent's that provides shield from radiant energy to the nitro chromophore, and amino auxochrome therefore, this effect conferred good light fastness properties on the dye (Sakoma *et al.*, 2012).

5.13 Perspiration Fastness

Both alkaline and acid perspiration test were evaluated and the results of the perspiration fastness test (Tables 4.6.6 and 4.6.7) shows that both acidic and alkaline perspiration were good to very good. Almost all the dyes gave a rating of 4 – 5 for change in colour and staining of adjacent fabric. The good perspiration fastness of the dyes may be due to the state of the dyes in the fabrics being in form of insoluble particle which resist attack of the chemicals in aqueous solution. From the results obtained it can be found that the rating in the acidic condition was slightly higher than in the alkaline condition, for both nylon 6 and polyester fabrics.

5.14 Fastness to Hot Pressing

The Hot press fastness of the synthesised dyes on nylon 6 and polyester fabrics was evaluated according to ISO and the results are shown in Tables 4.6.4 and 4.6.5. From the results obtained, it was observed that both nylon 6 and polyester gave a very good to excellent fastness to pressing. The results it shows that the synthesised dyes had a very good pressing fastness, rating of 4 – 5. The heat fastness of dyeing of equal dye concentration on the same substrate will, at a specific temperature and time, be dependent on the size and polarity of the molecules of the dye within the substrate and the volatility of the molecules of the dyes involved which in tend determines the rate of diffusion of the dye within the substance and the volatility of the dye (Sakoma *et al.*, 2012). Generally the hot pres fastness of the synthesised dyes on nylon 6 and polyester gave a very good to excellent result. This may be due to the chemical structure of the fabric as well as the chemical structure of the dyes (Shakra and Ali, 1992)

CHAPTER SIX

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATION

6.1 Summary

Squarylium dyes with high molecular weight, ranged from 296 and 468g/mol, high molar extinction coefficient, ranged from 5.2812 and $9.3962 \times 10^5 \text{ L mol}^{-1}\text{cm}^{-1}$ and good percentage dye exhaustion values ranging from 55 to 92 % and percentage yield of 53 to 97 % were successfully synthesised. FT-IR analysis was used to confirm all the various functional groups presents. GC-MS was used to elucidate the molecular mass of the synthesised dyes ranging from 296 and 468 g/mol. UV spectral analysis show that all the dyes were bathochromic. The result obtained from the study of pH on nylon 6 gave higher exhaustion at pH 6, at 100°C for 60 min, for polyester fabric, the effect of carrier concentration showed that carrier concentration of 1.25 g/L gave the highest exhaustion (91%) at 100°C for 60 min. The exhaustion was found to be better on nylon than polyester fabric, this may be attributed the crystalline and compact nature of polyester. The fastness properties of the synthesised dyes applied on nylon 6, and polyester fabrics gave good (4) to very good (5) result on wash fastness, light fastness was between 6 (very good) and 5 (good), perspiration was good very good (4) and (5) excellent, Hot pressing was found to be good (4) and very good (5), respectively.

6.2 Conclusions

FT-IR was used to confirm the functional groups of the synthesised dyes whereas the molecular masses were also established. Other physical properties of the synthesised dyes such as melting point and percentage yield were determined. These dyes give mostly red and yellow colour, crystalline in nature and insoluble in water. The

synthesised dyes were successfully applied to nylon 6 and polyester fabrics, from the fastness properties obtained at various pH, time and temperature for nylon 6. Effect of carrier concentration, time and temperature were investigated on polyester fabric. The result shows that increase in pH of dye – bath results in increase in exhaustion, depth of shade and dye uptake for the dyed samples, best dye exhaustion was achieved at pH 6, 100°C, and 60 min for the effect of pH , temperature and time on nylon 6, while polyester, best exhaustion and dye uptake was achieved at carrier concentration of 1.25 g/L (using phenol as carrier), 100°C at 60 min. Generally, level dyeing and best exhaustion, good wash and light fastness was observed on nylon 6 fabric. The good wash fastness observed on nylon 6 for dyes A, B, E, F, and I for nylon 6 may be attributed to the substituents such as OH, NO₂, N-H, respectively, and the hydrogen bond that bind the nylon 6 fabric and the dye together ,while for polyester fabric, very good wash fastness was achieved, which may be attributed to the crystalline nature of the polyester fabrics which made the dye molecules to penetrate the dyes with difficulty but when the dye molecules are in the fabric it is difficult to diffuse out. However, poor attraction and retention of the dyes were observed in dyes C, D, and H. This may be attributed to the halogens and methoxy group, substituents such as Br, Cl and OCH₃, respectively, found in the dye structure, which are electron withdrawing. It can be concluded that squarylium dyes can be applied to nylon 6 and polyester fabrics.

6.3 Recommendation

It is recommended that squarylium dyes could be applied to other synthetic textile fibres, such nylon 6.6, silk, and other modified synthetic fibres.

6.4 Contribution to Knowledge

New series of squarylium dyes that absorbed in the visible region of the spectrum have been synthesised with λ_{max} 435 – 500 nm in DMF

The dyes showed good exhaustion in nylon 6 and polyester with % exhaustion ranging from 57 – 92 %.

The dyes gave good to very good fastness properties such as wash fastness (4) and (5) on both nylon 6 and polyester fabrics, respectively.

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APPENDIX

Table 4.7: Effect of Dye Bath pH on % Exhaustion on nylon 6 using Dyes A - I

Dyes	pH 2	pH 3	pH 4	pH 5	pH 6	pH 8	pH 9	pH 10	pH 11	pH 12
A	48	71	83	87	92	60	47	44	41	40
B	50	66	69	75	80	57	47	43	40	41
C	24	25	27	30	37	22	20	21	19	18
D	25	26	28	30	38	24	23	22	21	20
E	64	57	66	69	84	62	55	50	45	43
F	51	62	66	73	86	77	66	55	52	50
G	47	50	56	60	68	46	44	43	42	39
H	24	26	27	29	33	23	22	21	20	19
I	63	65	68	75	82	68	55	47	43	40

Table 4.8: Effect of Time on Dyeing on nylon 6 % Exhaustion using Dyes A-I

Dyes	10 min	20 min	30 min	40 min	50 min	60 min
A	33	42	45	50	64	85
B	20	25	36	42	57	78
C	20	21	25	27	28	30
D	19	22	24	26	27	31
E	21	28	43	50	62	71
F	28	30	50	57	60	92
G	25	30	36	39	40	46
H	21	23	25	27	28	30
I	26	35	40	44	71	74

Table 4.9: Effect of temperature on % Exhaustion of nylon 6 using Dyes A-I

Dyes	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
A	42	50	64	77	79	83	85
B	36	42	50	71	75	79	84
C	21	22	24	25	27	29	30
D	14	19	21	25	26	30	33
E	40	57	66	78	83	85	88
F	57	64	71	79	85	82	94
G	28	30	31	50	57	58	60
H	12	15	20	22	25	27	30
I	45	50	60	68	71	76	84

Table 4.10: Effect of carrier concentration on % Exhaustion of polyester using Dyes A-I

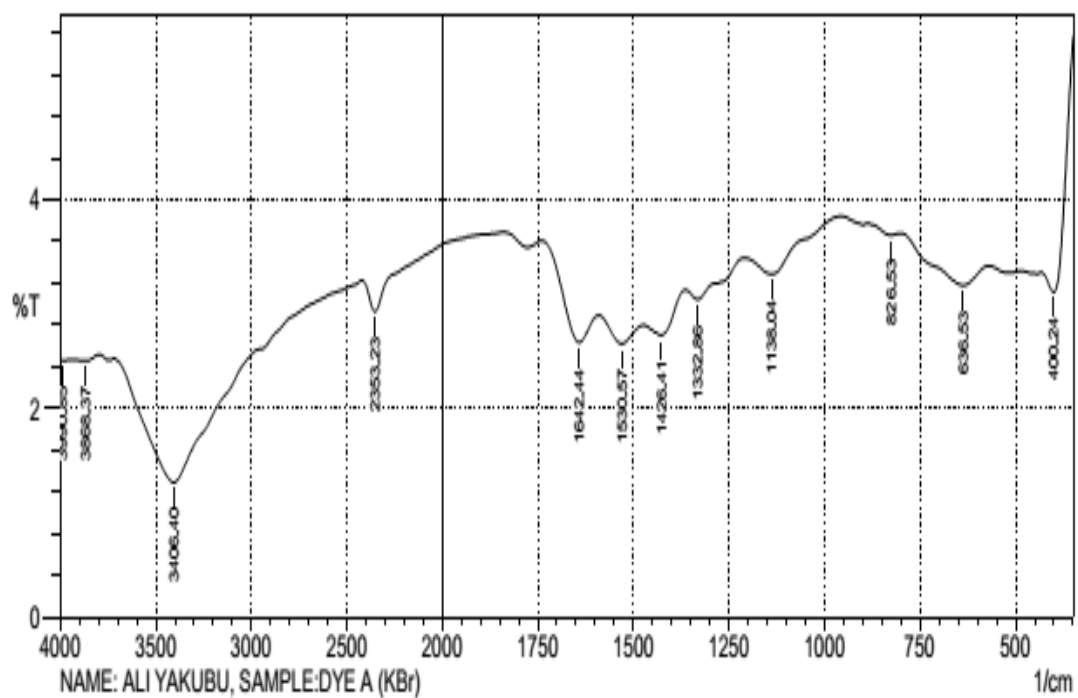
Dyes	0.25 g/L	0.5 g/L	0.75 g/L	1 g/L	1.25 g/L
A	41	47	55	59	61
B	47	50	56	65	67
C	22	25	26	28	30
D	24	26	28	30	32
E	64	71	75	86	91
F	70	73	77	81	88
G	41	43	45	57	64
H	23	25	29	35	37
I	57	64	71	80	82

Table 4.11: Effect of temperature on %Exhaustion of polyester using Dyes A-I

Dyes	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
A	42	52	57	60	63	65	68
B	44	53	58	62	71	76	78
C	21	23	25	26	27	29	31
D	23	25	26	28	30	32	35
E	48	62	67	74	77	81	87
F	54	61	66	72	79	82	85
G	47	59	64	69	72	75	76
H	18	21	26	29	32	37	39
I	45	56	64	68	73	78	80

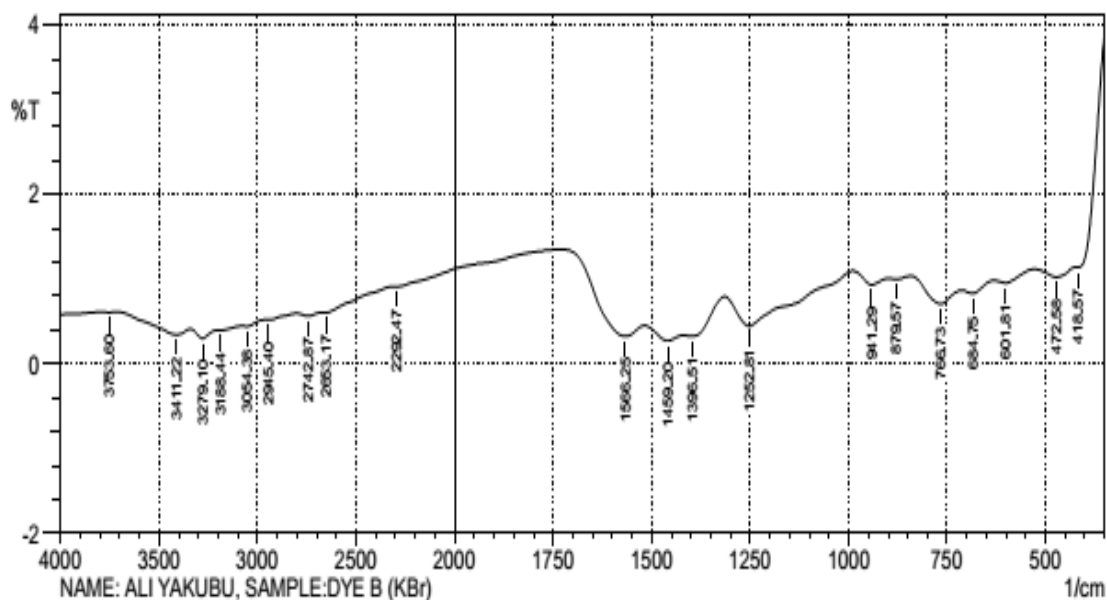
Table 4.12: Effect of time on % Exhaustion of polyester using Dyes A-I

Dyes	10 min.	20 min.	30 min.	40 min.	50 min.	60 min.
A	17	25	38	44	55	66
B	20	30	40	47	60	73
C	14	28	30	32	34	35
D	27	30	31	33	34	36
E	29	36	42	50	67	83
F	21	35	43	57	71	79
G	13	25	37	39	50	62
H	12	18	20	25	31	35
I	31	37	41	52	68	74



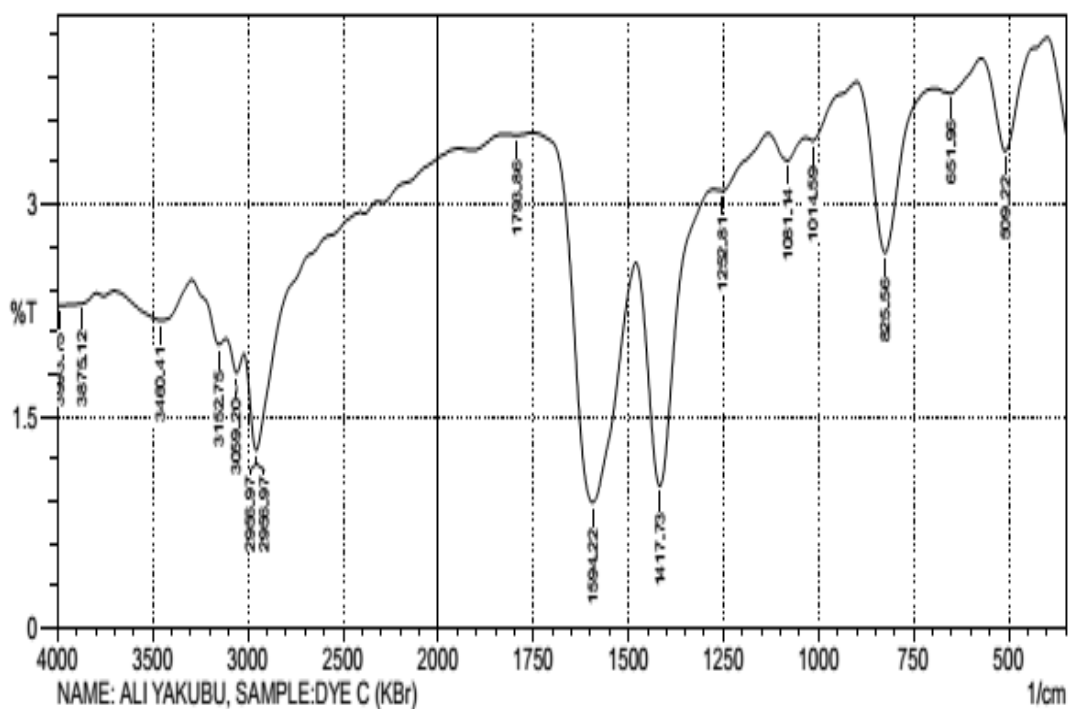
	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	400.24	3.119	1.072	433.03	349.13	120.5	5.77
2	636.53	3.185	0.278	801.45	569.02	342.33	4.639
3	826.53	3.665	0.045	885.36	801.45	120.053	0.184
4	1138.04	3.29	0.272	1209.41	956.72	366.605	3.071
5	1332.86	3.05	0.155	1364.68	1209.41	231.891	1.708
6	1426.41	2.711	0.238	1473.66	1364.68	168.485	1.994
7	1530.57	2.625	0.224	1590.36	1473.66	182.361	2.042
8	1642.44	2.64	0.509	1738.89	1590.36	226.083	4.787
9	2353.23	2.934	0.352	2421.71	1841.12	852.902	4.337
10	3406.4	1.299	1.361	3714.06	2421.71	2122.482	121.892
11	3868.37	2.463	0.005	3874.16	3794.11	128.399	0.064
12	3990.85	2.467	0.001	3995.67	3960.96	55.812	0.003

Figure 4.4.1: FTIR spectrum of Dye A



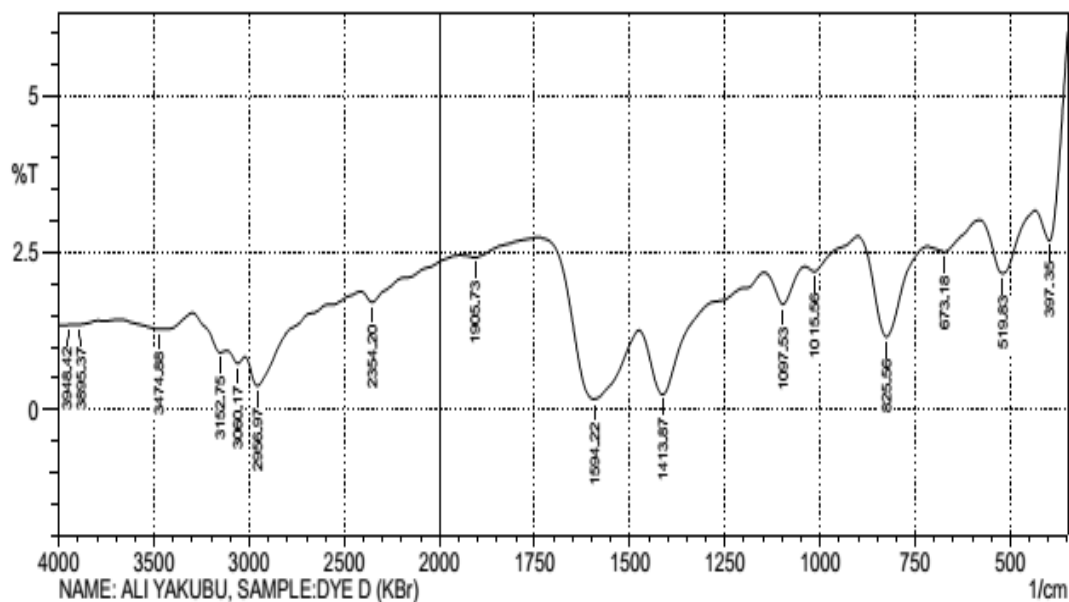
	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	418.57	1.1433	0.1821	423.39	349.13	128.1307	4.2951
2	472.58	1.0239	0.1085	527.55	424.35	203.0635	2.2169
3	601.81	0.957	0.0673	629.78	528.51	201.5195	1.2749
4	684.75	0.8362	0.0736	712.72	630.74	167.9207	1.3169
5	766.73	0.7085	0.2311	841.96	713.69	266.6876	7.2901
6	879.57	1.0039	0.0185	897.89	842.92	109.5493	0.2339
7	941.29	0.9364	0.1188	988.55	898.86	179.4239	2.1715
8	1252.81	0.449	0.4047	1314.53	989.52	695.6923	36.3973
9	1396.51	0.3285	0.1075	1418.69	1315.5	240.3307	5.126
10	1459.2	0.2755	0.1104	1518.03	1419.66	243.0816	6.4002
11	1566.25	0.3287	0.3275	1732.13	1518.99	464.213	19.4395
12	2292.47	0.916	0.0132	2308.87	1733.1	1125.2185	1.9808
13	2653.17	0.6112	0.0179	2672.46	2309.83	768.1998	0.7868
14	2742.87	0.5655	0.0408	2801.7	2673.43	286.2248	1.8569
15	2945.4	0.5236	0.0079	2960.83	2802.66	356.4998	0.533
16	3054.38	0.4478	0.0194	3079.46	2961.8	272.8205	0.9333
17	3188.44	0.3959	0.0057	3200.01	3080.42	284.162	0.458
18	3279.1	0.3061	0.0993	3339.86	3200.98	339.7944	7.4023
19	3411.22	0.3476	0.1042	3710.2	3340.82	864.3366	16.204
20	3753.6	0.6126	0.0061	3792.18	3711.17	179.0882	0.1673

Figure 4.4.2: FTIR spectrum of Dye B



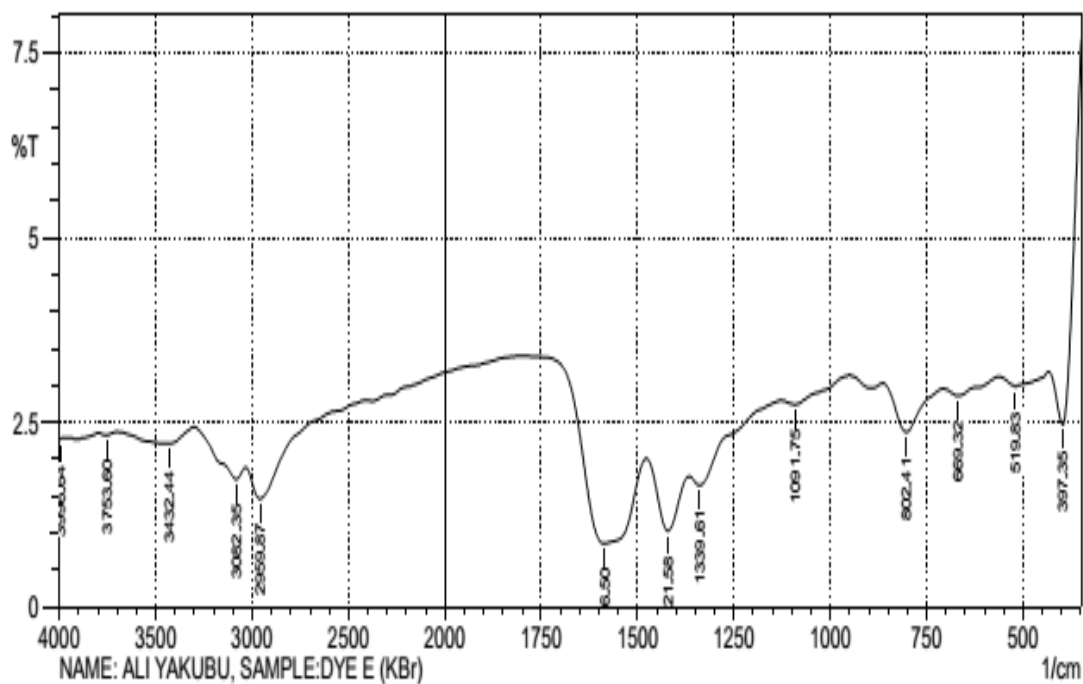
	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	509.22	3.3794	0.7114	572.88	400.24	244.5153	5.1984
2	651.96	3.7905	0.1068	694.4	572.88	171.6326	0.8015
3	825.56	2.6598	1.1931	899.82	694.4	302.2328	11.5604
4	1014.59	3.4571	0.0749	1034.84	899.82	193.8593	-0.0059
5	1081.14	3.3123	0.1753	1132.25	1034.84	143.0125	1.0503
6	1252.81	3.1024	0.0686	1274.99	1132.25	211.9524	0.511
7	1417.73	1.0103	1.7396	1480.42	1274.99	344.0878	26.3295
8	1594.22	0.8938	2.0858	1750.46	1480.42	458.6188	48.0394
9	1793.86	3.4924	0.0127	1823.76	1753.35	102.5118	0.0601
10	2956.97	1.2621	0.7898	3021.59	2409.17	1002.6936	10.1119
11	2956.97	1.2621	0.7898	3021.59	2409.17	1002.6936	10.1119
12	3059.2	1.81	0.1787	3115.14	3021.59	160.7333	1.7588
13	3152.75	2.0102	0.1281	3295.49	3115.14	298.1443	0.964
14	3460.41	2.1826	0.0009	3674.52	3459.45	353.7071	0.5046
15	3875.12	2.2998	0.0029	3878.01	3796.04	133.8022	0.0556
16	3993.75	2.2875	0.0008	4000.5	3987.96	20.5689	0.0012

Figure 4.4.3: FTIR spectrum of Dye C



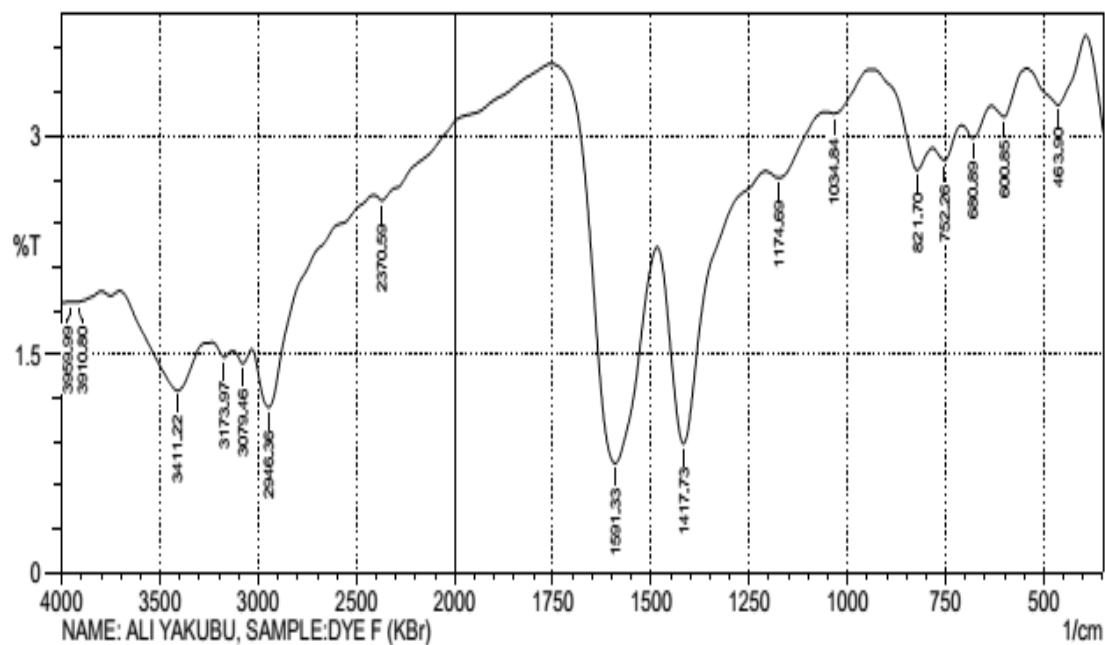
	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	397.35	2.6921	1.7248	434.96	349.13	125.7151	8.9984
2	519.83	2.169	0.9162	581.56	434.96	230.9668	9.7301
3	673.18	2.5074	0.2274	718.51	581.56	214.9406	2.2589
4	825.56	1.162	1.5287	900.79	718.51	311.5849	24.9144
5	1015.56	2.1995	0.1655	1040.63	900.79	225.1399	1.2859
6	1097.53	1.6812	0.5481	1147.68	1040.63	182.4413	5.659
7	1413.87	0.2424	1.1704	1476.56	1196.87	548.8128	43.6684
8	1594.22	0.1725	1.7503	1738.89	1476.56	545.4899	91.404
9	1905.73	2.427	0.0844	1946.24	1742.74	323.3574	0.5374
10	2354.2	1.7135	0.2418	2414.96	1946.24	789.2497	7.5467
11	2956.97	0.3817	0.5827	3021.59	2578.91	883.6102	31.5059
12	3060.17	0.7352	0.1456	3119	3021.59	203.1308	3.364
13	3152.75	0.9101	0.1422	3299.35	3119	347.873	1.7275
14	3474.88	1.2808	0.0007	3674.52	3473.91	374.8027	0.0914
15	3895.37	1.355	0.0013	3897.3	3793.14	193.6059	0.0366
16	3948.42	1.3478	0.0004	3950.35	3912.73	70.3189	0.002

Figure 4.4.4: FTIR spectrum of Dye D



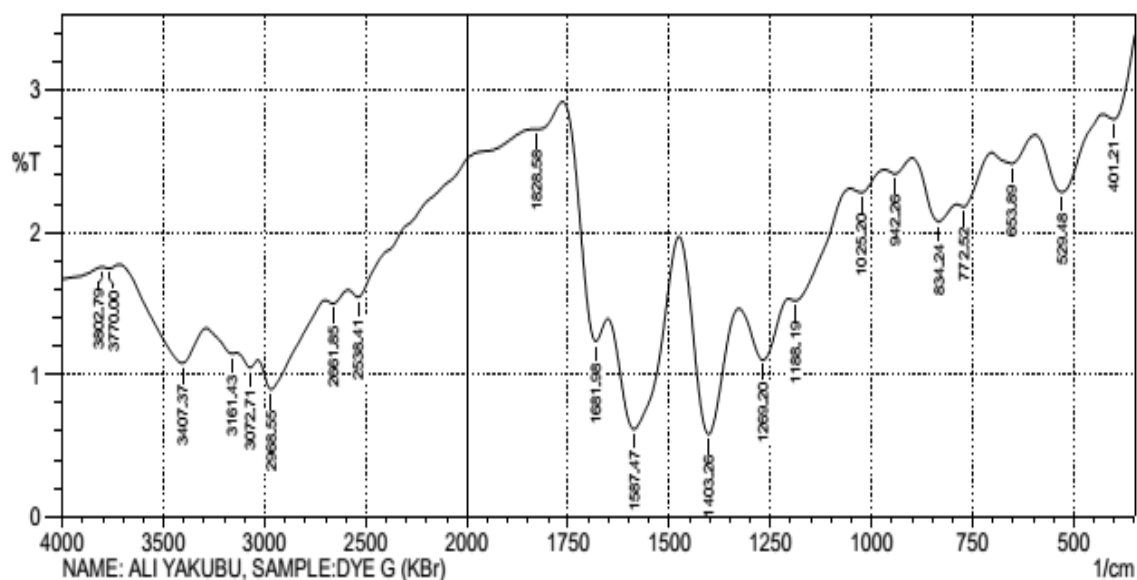
	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	397.35	2.468	2.629	433.03	349.13	121.465	11.912
2	519.83	2.994	0.149	562.27	433.03	195.7	1.701
3	669.32	2.857	0.108	706.93	620.13	133.257	0.66
4	802.41	2.369	0.631	864.14	706.93	246.339	6.756
5	1091.75	2.745	0.119	1128.39	950.94	272.826	1.542
6	1339.61	1.647	0.244	1366.61	1128.39	391.638	-1.975
7	1421.58	1.033	0.86	1477.52	1366.61	204.314	13.152
8	1586.5	0.859	1.664	1771.68	1477.52	512.418	46.79
9	2959.87	1.469	0.53	3033.16	2407.24	1032.429	7.185
10	3082.35	1.732	0.262	3300.31	3033.16	452.728	7.109
11	3432.44	2.212	0.057	3473.91	3300.31	284.74	1.093
12	3753.6	2.329	0.006	3759.39	3706.34	86.43	0.027
13	3996.64	2.282	0.001	4000.5	3970.6	49.071	0.002

Figure 4.4.5: FTIR spectrum of Dye E



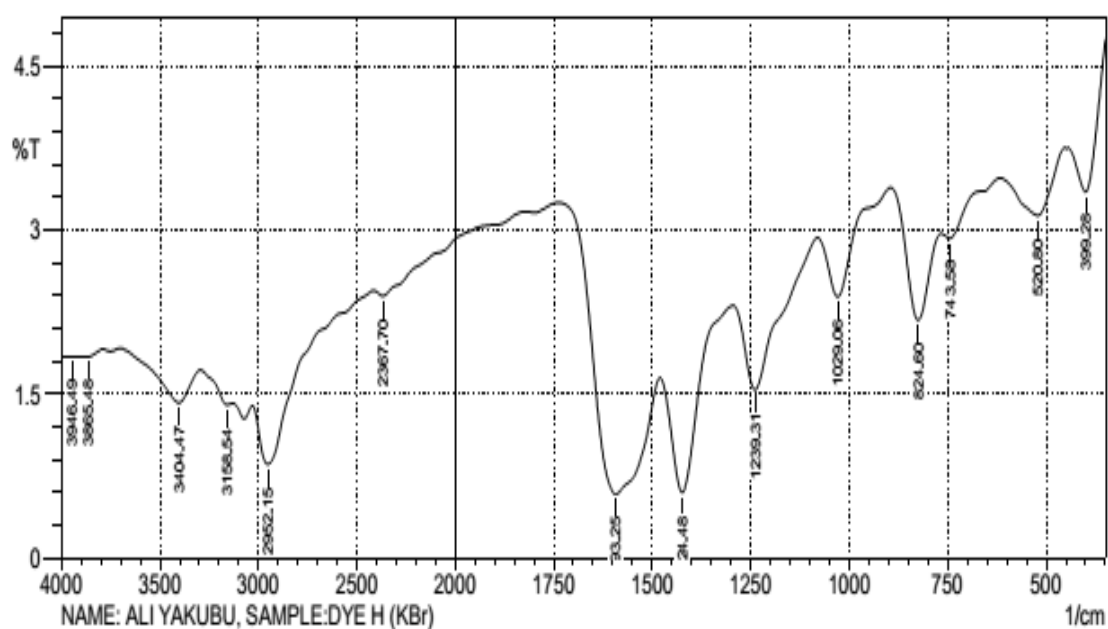
	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	463.9	3.2158	0.3725	543.94	392.53	222.8178	3.8484
2	600.85	3.1357	0.1691	633.64	543.94	133.249	0.7995
3	680.89	2.9909	0.1375	709.83	633.64	115.1883	0.7084
4	752.26	2.8362	0.1519	784.09	709.83	113.8909	0.7801
5	821.7	2.7701	0.2841	937.44	784.09	231.0539	1.4259
6	1034.84	3.1581	0.0647	1057.03	937.44	177.4241	0.4503
7	1174.69	2.7175	0.1347	1208.44	1057.03	232.7989	1.2783
8	1417.73	0.8873	1.4797	1485.24	1208.44	474.513	30.447
9	1591.33	0.7522	1.9845	1754.32	1485.24	470.2485	52.4078
10	2370.59	2.5614	0.095	2412.06	1754.32	1004.8156	4.7092
11	2946.36	1.1392	0.5477	3033.16	2412.06	1062.4124	7.1765
12	3079.46	1.4401	0.0915	3129.61	3033.16	176.3105	1.2703
13	3173.97	1.4821	0.067	3234.73	3129.61	191.0227	0.883
14	3411.22	1.2535	0.4386	3706.34	3273.31	787.8264	26.836
15	3910.8	1.8649	0.0006	3911.77	3798.93	194.3107	0.0918
16	3959.99	1.8617	0.0001	3960.96	3954.2	11.6798	0.0001

Figure 4.4.6: FTIR spectrum of Dye F



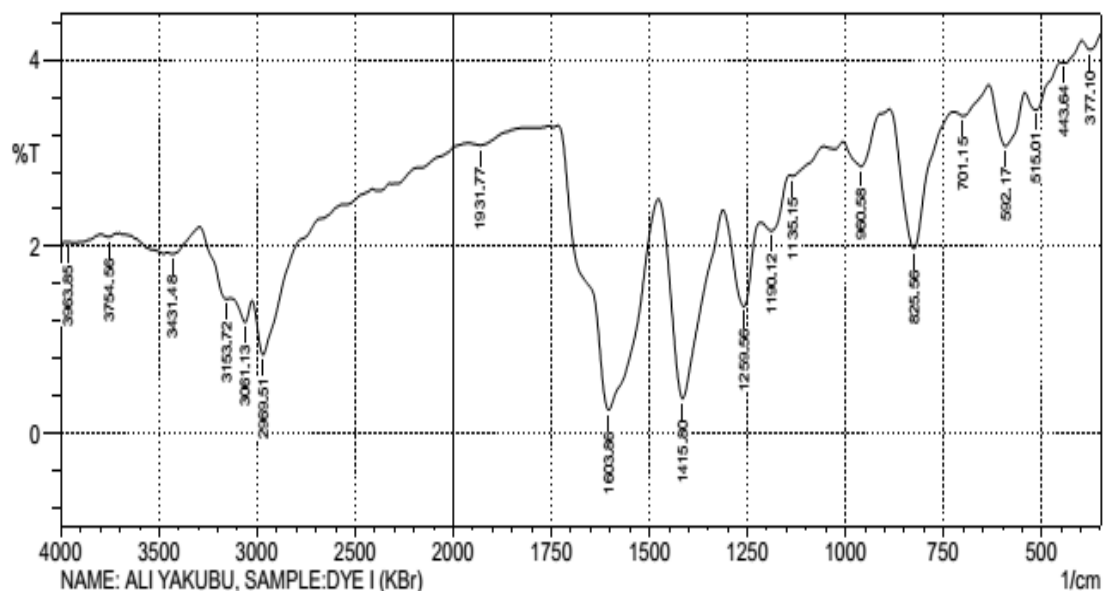
	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	401.21	2.7976	0.2255	428.21	349.13	121.0925	1.8073
2	529.48	2.2842	0.4597	595.06	429.18	264.8864	6.2292
3	653.89	2.4856	0.1322	703.08	596.02	170.5337	1.2587
4	772.52	2.1799	0.088	788.91	704.04	138.482	0.6844
5	834.24	2.0777	0.2509	899.82	789.88	181.6136	2.6016
6	942.26	2.4126	0.06	968.3	900.79	108.7327	0.3653
7	1025.2	2.2817	0.0697	1052.2	969.26	135.2214	0.5026
8	1188.19	1.5182	0.099	1204.59	1053.17	262.8906	2.0917
9	1269.2	1.1012	0.3961	1328.03	1205.55	231.2474	7.794
10	1403.26	0.5794	1.1417	1475.59	1329	289.1252	29.6186
11	1587.47	0.6156	0.9879	1651.12	1476.56	347.8186	37.0455
12	1681.98	1.2337	0.567	1763.96	1652.09	195.3044	6.2504
13	1828.58	2.7266	0.0111	1832.44	1764.93	104.8978	0.3096
14	2538.41	1.5451	0.1246	2587.59	1836.29	1256.3413	2.1375
15	2661.85	1.5003	0.0476	2701.4	2588.56	204.6882	0.7701
16	2968.55	0.8972	0.2857	3033.16	2702.36	640.82	16.4131
17	3072.71	1.0495	0.0702	3140.22	3034.13	208.022	1.3313
18	3161.43	1.1493	0.0273	3288.74	3141.18	282.1546	0.6618
19	3407.37	1.0806	0.3693	3711.17	3289.7	789.8986	25.0758
20	3770	1.7474	0.0063	3778.68	3725.63	93.1059	0.063
21	3802.79	1.7561	0.0007	3805.68	3799.89	10.1577	0.0005

Figure 4.4.7: FTIR spectrum of G



	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	399.28	3.355	0.866	443.64	349.13	134.91	5.005
2	520.8	3.138	0.504	616.28	452.32	241.745	5.386
3	743.58	2.93	0.132	766.73	665.46	152.38	0.467
4	824.6	2.182	0.981	894.04	766.73	199.617	8.896
5	1029.06	2.397	0.665	1081.14	894.04	286.863	6.038
6	1239.31	1.544	0.935	1295.24	1081.14	355.72	16.648
7	1424.48	0.604	1.249	1480.42	1295.24	341.863	25.492
8	1593.25	0.588	1.767	1737.92	1480.42	481.521	60.584
9	2367.7	2.402	0.104	2413.99	1820.86	925.134	3.233
10	2952.15	0.863	0.67	3031.23	2413.99	1087.784	18.337
11	3158.54	1.407	0.064	3294.53	3131.54	294.702	0.432
12	3404.47	1.427	0.352	3700.56	3294.53	721.873	15.595
13	3865.48	1.847	0.002	3867.4	3791.21	131.525	0.055
14	3946.49	1.848	0.001	3954.2	3936.84	30.088	0.002

Figure 4.4.8: FTIR spectrum of Dye H



	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	377.1	4.1201	0.1269	398.31	349.13	67.8582	0.4023
2	443.64	3.9704	0.0465	452.32	398.31	75.2148	0.269
3	515.01	3.4674	0.2886	542.98	452.32	130.1041	1.4987
4	592.17	3.0787	0.6215	634.6	542.98	135.3886	4.1721
5	701.15	3.4056	0.1176	724.29	634.6	130.3736	0.7785
6	825.56	1.9799	1.4855	887.28	724.29	253.3907	15.317
7	960.58	2.8654	0.3955	1006.88	887.28	179.9269	2.6887
8	1135.15	2.7617	0.0284	1141.9	1055.1	133.5672	0.3196
9	1190.12	2.1719	0.2653	1216.16	1141.9	120.9844	2.0129
10	1259.56	1.3584	0.9613	1312.6	1216.16	167.7892	10.2481
11	1415.8	0.3689	2.0989	1477.52	1312.6	314.2388	48.6411
12	1603.86	0.2486	2.6506	1734.06	1477.52	493.4947	98.2052
13	1931.77	3.088	0.0614	1962.64	1818.93	215.2757	0.3628
14	2969.51	0.8378	0.7072	3025.45	2561.55	816.6001	14.5067
15	3061.13	1.1894	0.2387	3135.39	3025.45	206.38	3.6332
16	3153.72	1.4395	0.0928	3293.56	3135.39	277.6769	1.2006
17	3431.48	1.9242	0.0524	3457.52	3293.56	277.3423	1.1384
18	3754.56	2.101	0.0244	3774.82	3716.95	96.8863	0.1568
19	3963.85	2.0472	0.0024	3971.56	3959.03	21.171	0.0035

Figure 4.4.9: FTIR spectrum of Dye I

GC-MS ANALYSIS

ALI YAKUBU (SAMPLE -DYE A)

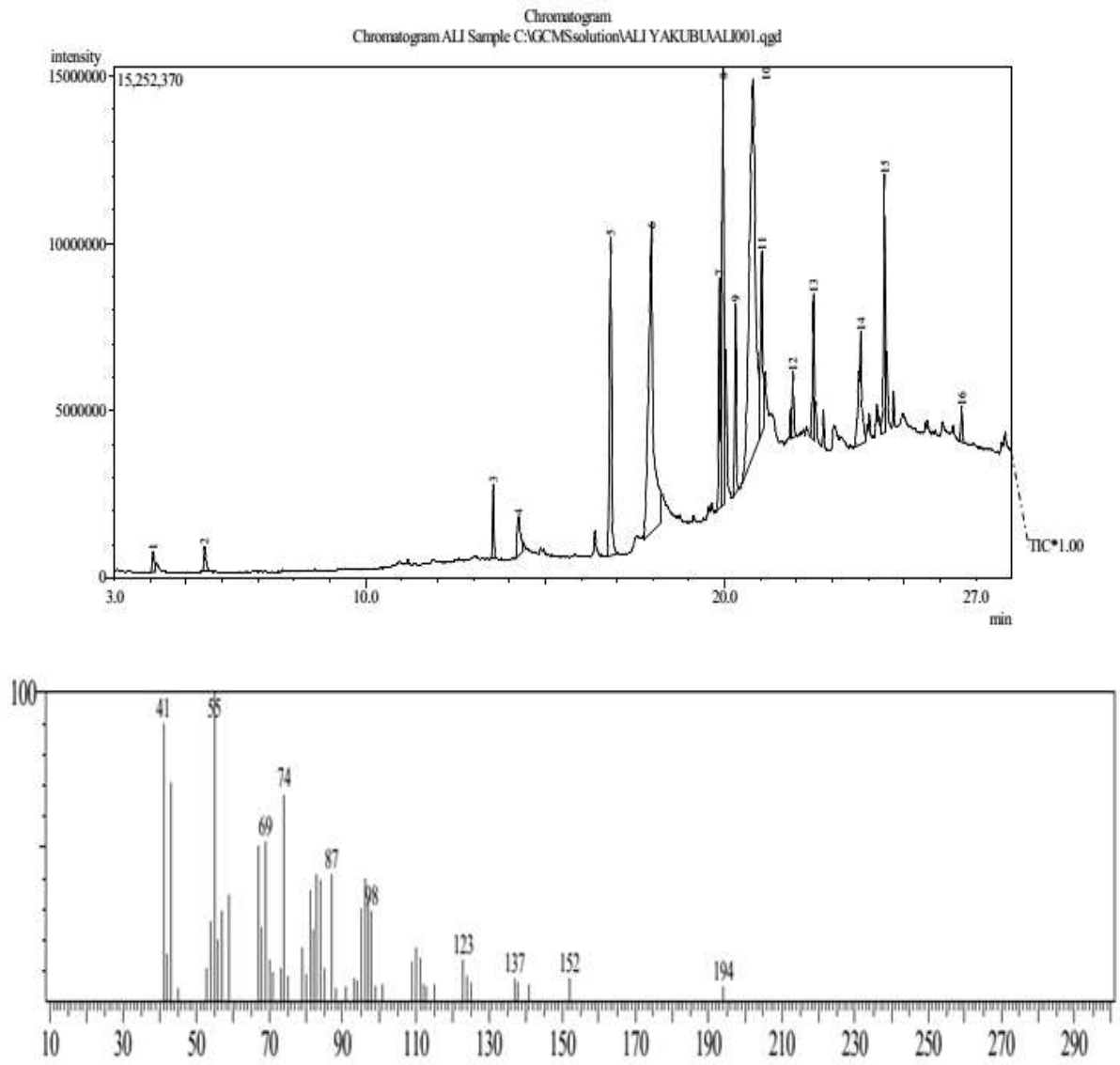


Figure 4.5.1: GC-MS spectrum of Dye A

ALI YAKUBU (SAMPLE -DYE B)

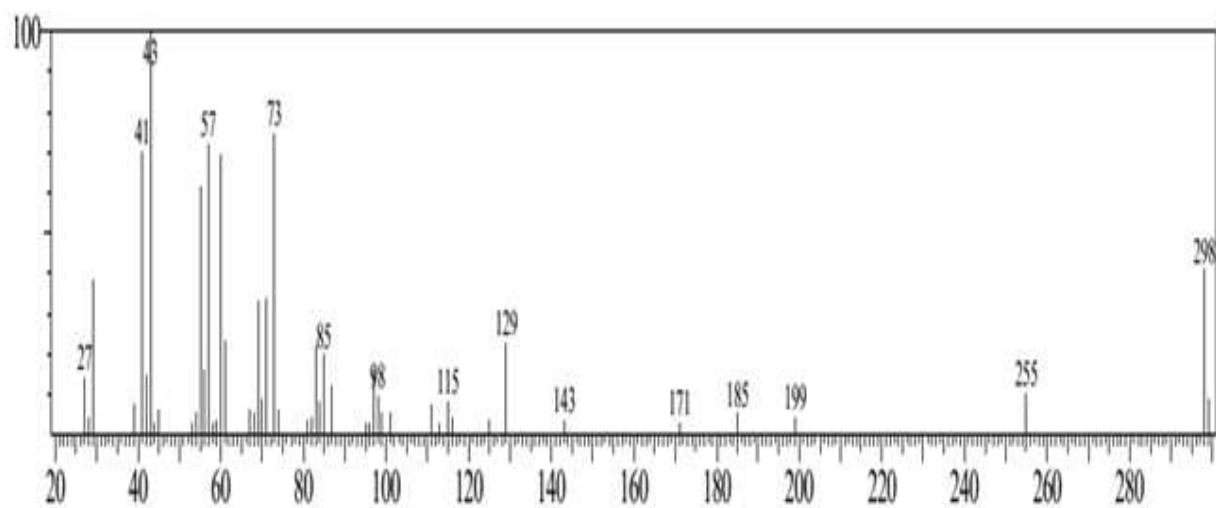
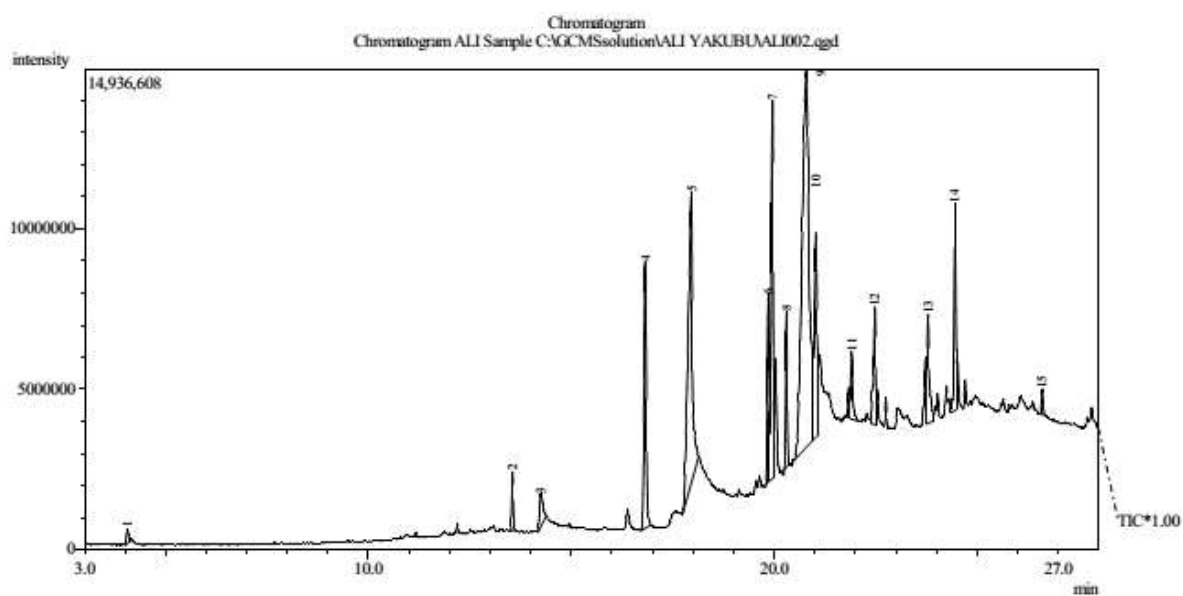


Figure 4.5.2: GC-MS spectrum of Dye B

ALI YAKUBU (SAMPLE -DYE F)

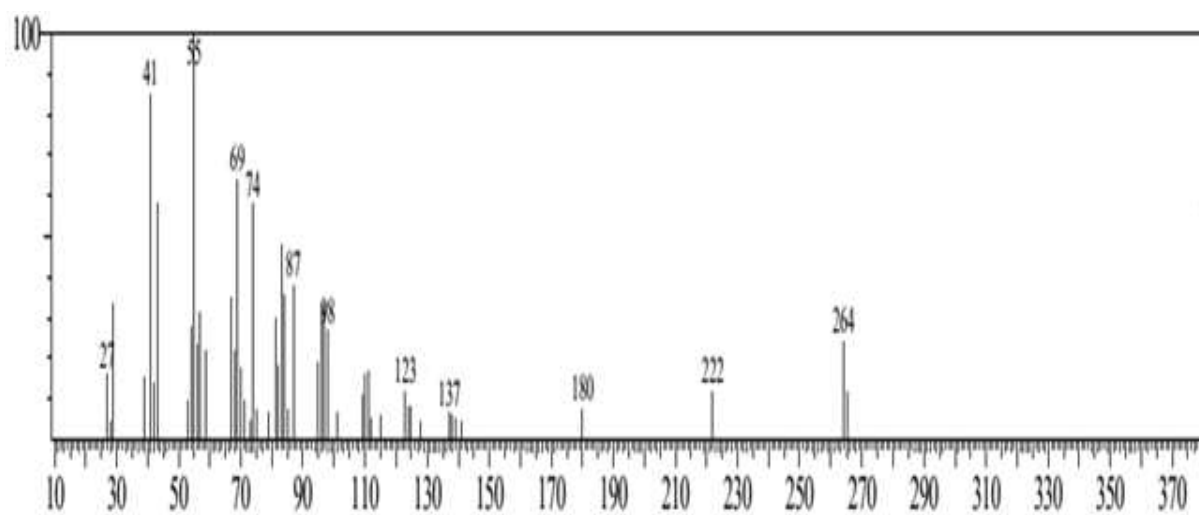
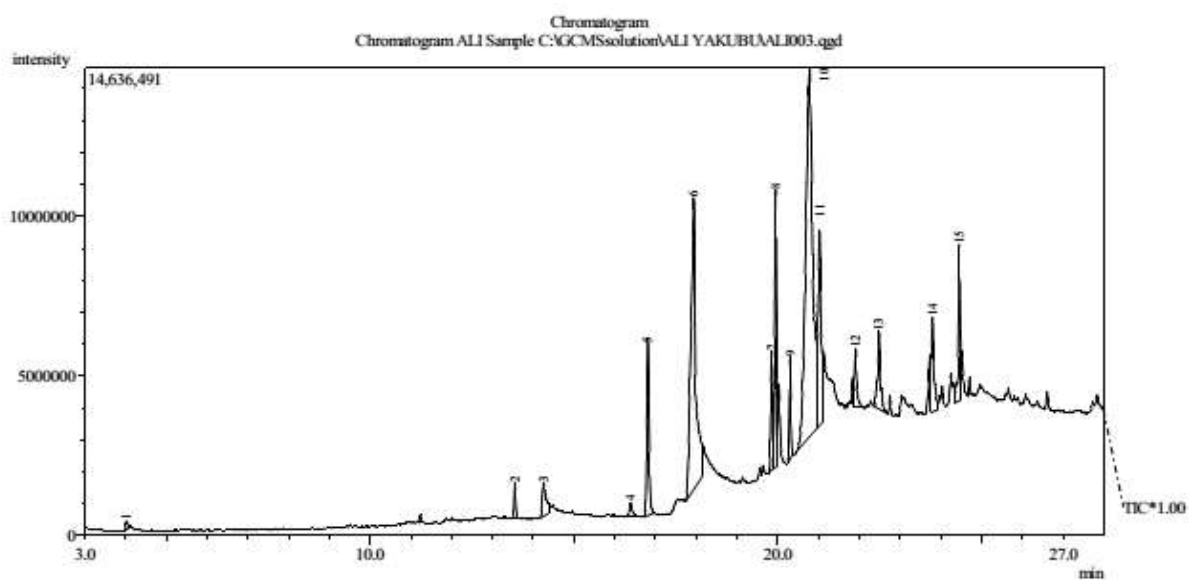


Figure 4.5.3: GC-MS spectrum of Dye F

ALI YAKUBU (SAMPLE -DYE H)

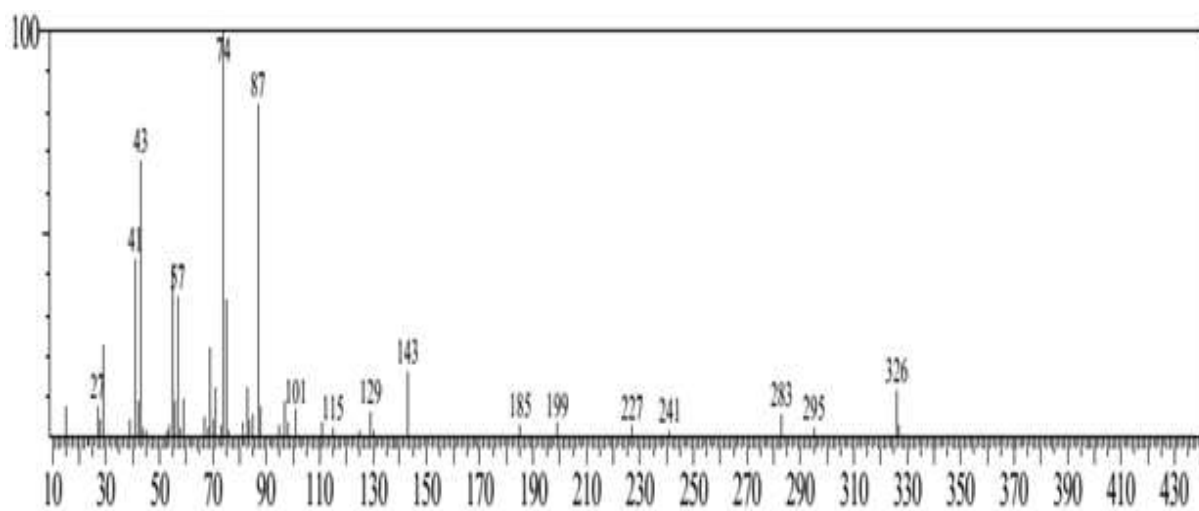
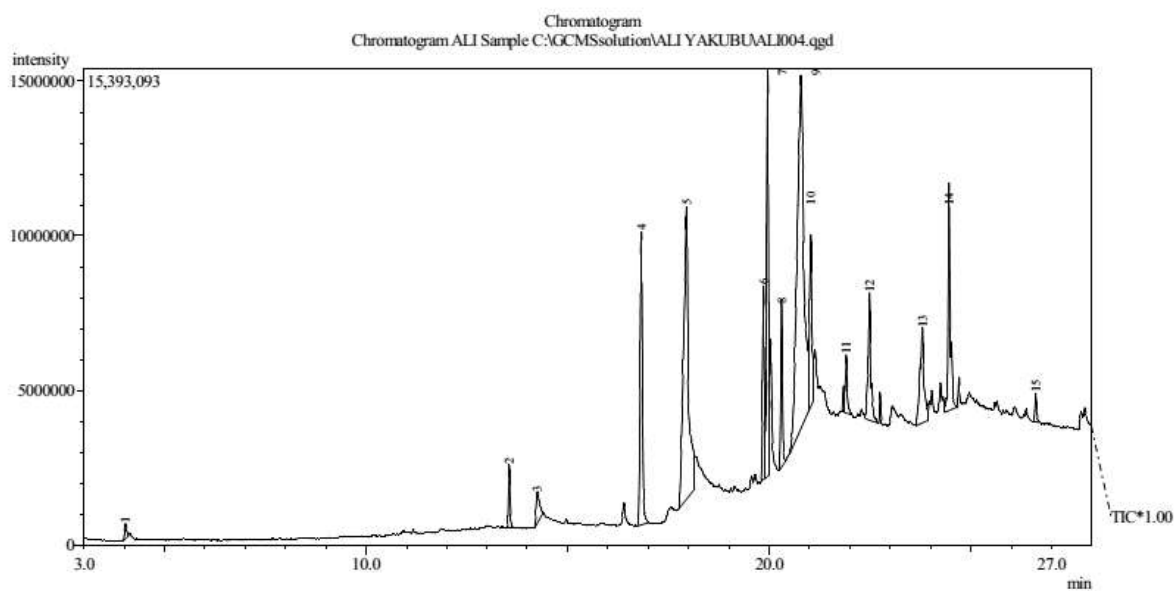


Figure 4.5.4: GC-MS spectrum of Dye H



Plate I: Synthesis setup for Dye A



Plate II: Synthesis setup for Dye B



Plate III: Dyed samples (N – Nylon 6; P – Polyester)