

# Synthesis and Characterization of Di J Acid Urea Based Direct Dyes



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2014-UET-IEFR/M.Sc-CHEM/FD-11

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# **Dedication**

**“This work is dedicated to my family ”**

# **Synthesis and Characterization of Di J Acid Urea Based Direct Dyes**

This thesis is being submitted to Chemical Engineering Department, NFC Institute of Engineering & Fertilizer Research Faisalabad in partial fulfillment of

**Master's Degree**

**In**

**Chemical Engineering**

Approved on: \_\_\_\_\_

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**Internal Examiner**

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**External Examiner**

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**Chairman/ Director of Institution**

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**Dean of the Faculty**

## *Acknowledgement*

I want to express my gratitude to **Almighty Allah** “Who teaches man by pen, teaches which he knew out” for His special grace upon us Prophet and to the **Holy Prophet Muhammad (S.A.W)** who showed light of knowledge to the humanity as a whole.

My sincere thanks broaden to my project advisor **Prof. Dr. Shahid Raza Malik** (Director, NFC Institute of Engineering & Fertilizer Research, Faisalabad) for his invaluable advice, encouragement, technical discussions, inspiring guidance, remarkable suggestions, keen interest which enabled me to complete this research work.

I feel much pleasure to avail this opportunity to express deep sense of gratefulness to **Dr. Waqar Ali Khan**(Associate Professor, Chemical Engineering Department, NFC-IEFR, Faisalabad) and for their beneficial suggestions, commendable discussions and pedagogic guidance to bring this work to accomplishment.

I am grateful to Mr. Abbas CEO Haris Dyes for guiding me to this research work and providing me logistic support in terms of providing me necessary chemicals, Labs and testing facility.

No words to express my humble obligation to my friend Mr.Shabbir for their valuable guidance, encouragement and support for my success.

At last again many thanks to all who have been attached with me for the completion of my project and who prayed for my success.

## **Abstract:**

Textile industry is the back bone of Pakistan economy and largest contributor of country's export. It is anticipated that about 59% of the country's total export, 43% of industrial manufacture and 40% of employed industrial work force is being working in textile industry.

Textile sector consumed huge amount of Dyes and pigments, among them major market share are of pigments and reactive dyes. Approximately direct dyes have only 25 % market share. Being relatively cheap, easy to manufacture and application without any mordant ,direct dyes market share could be increase which will save foreign remittances.

Direct dyes based on di J acid urea have been synthesid and characterized in order to investigate the fastness, color strength and substantivity. Various characterization techniques like UV-Vis spectrophotometer (for  $\lambda$ ) and FTIR (For functional group)were deployed to check wavelength in visible spectra and ensure the required functionalized chromogens.

Fastness properties observed are of better quality by different ISO standards of fastness (Light,Washing,Crock) against temperature variation.

Color strength K/s studied by empirical relation of kubelka munk equation.improved results have been observed.

**Author**

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# 1 INTRODUCTION

Since several years, Direct Dyes are being incorporated. The Direct Dyes have a restricted degree, financially, as a result of the way that their wet-speed and light-quickness, both are poor, notwithstanding of their simple application. Thus by utilizing it alongside a stringent to make it color capable is the achievement that set an earth shattering change in cotton-coloring. So changes are made by acquainting new synthetic arrangements with defeat these restrictions. Cellulosic filaments were colored utilizing the Direct Dyes until 1950, when the reactive Dyes were presented, with a specific end goal to accomplish higher guidelines of wet-speed in material exchange. As the reactive Dyes have both extraordinary wet-quickness and fine light-speed, over a scope of splendid hues. Direct Dyes are under usage for some reasons anyplace high wet-speed is not required. For cellulosic strands, Direct Dyes are a standard class of colors. These are anionic and have a cellulosic strands connection. As the name demonstrates, the Direct Dyes can be connected specifically to the filaments without any obsession procedure, for example, mordanting. (CHRISTIE, 2001). Truly, these were utilized for cotton coloring, so these are emerge a direct cotton dyes. (KENT, 2007)

Direct Dyes are bestowed from an electrolyte containing fluid color shower. Straightforwardness is the most striking normal for this procedure, notwithstanding, till the end of a century ago, an after-treatment for increase of wet speed was essential. Other than material division, the Direct Dyes are likewise utilized for the calfskin coloring and the paper coloration. Indeed, even the after-treatment doesn't gather the extreme end utilizes as a part of cellulosic apparel and outfitting materials. so a large portion of them are substituted by reactive dyes. The procedure of sap completing enhances the wet-quickness, especially on strengthened cellulosic-textures. New levels have been accomplished in the setup of cross-connecting reactants and in the wake of treating operators, so the Direct Dyes may fight with reactive Dyes.

Direct Dyes are utilized as a part of sparing mixed and goeey decorations, window ornaments textures and floor coverings. Cheap attire that can be washed infrequently is typically colored utilizing direct colors. Another utilization of direct colors is in easygoing and rain-wear of cellulosic or mixed textures, that are sturdy and water-repellent.

## 1.1 Structure and properties of direct dyes for cellulose

Azo-groups goes about as a chromophore in the greater part of the Direct Dyess. Very nearly 75% of every Direct Dyes constitute un-metallised azo-bunches, that are connoted in each shading plan.

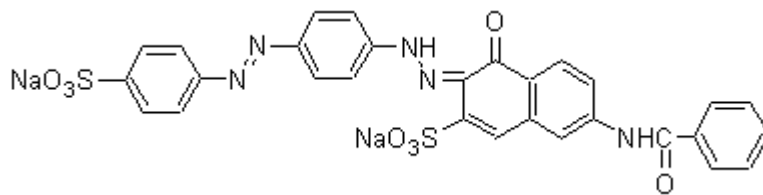
Disazo-aggregate or polyazo-bunch likewise constitute greater part of direct colors. Diazo-aggregate wins in the exceptional yellow to blue range and polyazo-gathering is operating at a profit, dim, greens and chestnut. From disazo and polyazo-subgroups, Cu-complex direct colors are inferred. Stilbene and thiazole based colors are the main non-azo-colors.

### 1.1.1 Chemical classification

On the premise of their structure, Direct Dyesare isolated into 4 fundamental chromophores,

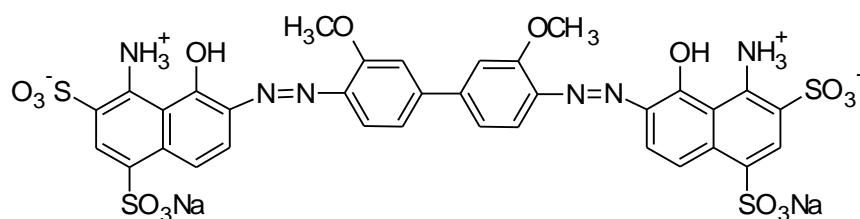
Sr. No.	Dye type	Examples
1	azo dyes	C.I Direct Red-81
2	Stilbenedyes	C.I-Direct Yellow-12
3	oxazine dyes	C.I. Direct Blue 106
4	phthalocyanine	C.I. Direct Blue 86

**Table 1.1 Direct Dyes Classification**



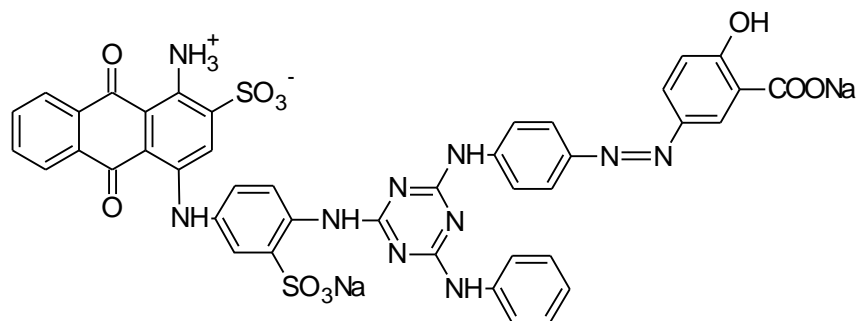
**Figure 1.1 Direct Red 81**

Around half of every Direct Dyes are disazo-goup. For instance, the symmetrical Dianisidine subordinate C.I. Coordinate Blue 1.



**Figure 1.2 Direct Blue 1**

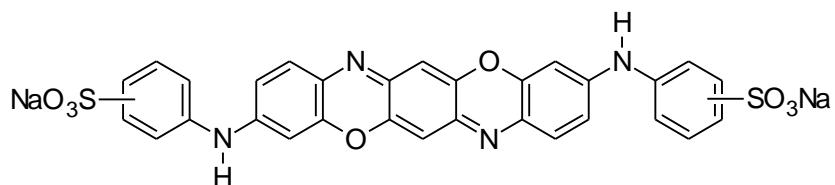
Another case is C.I. Coordinate Green 28, here a non-substantive Anthra-quinone Derivative is connected with a Substantive Phenyl-azosalicylic corrosive middle of the road by Cyanuric chloride.



**Figure 1.3 Direct Green 28**

An essential blue color like C.I. Coordinate Blue 106, depends on Tri-pheno-di-oxazine ring framework. As of late, anthra-quinone receptive colors, which are great however less financially savvy, were substituted by brilliant blue subsidiaries of phthalo-cyanine, tri-pheno-di-oxazine

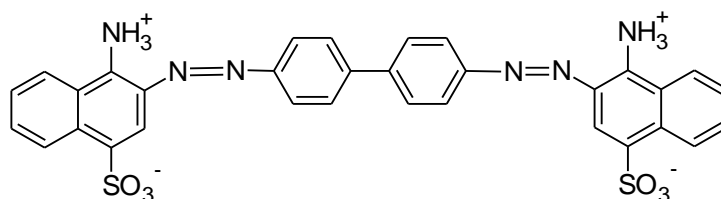
and formazan chromogens. Which are discovered compelling in yielding non-receptive precursors that are utilized as Direct Dyes.



**Figure 1.4 Direct Blue 106**

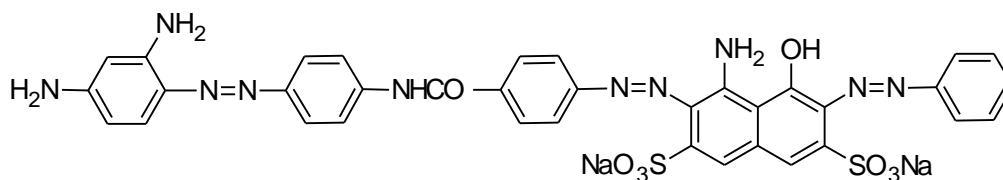
### 1.1.2 Replacements for benzidine-derived dyes

First business dye was Congo red or C.I. Coordinate Red 28, which of manufactured utilizing benzidine and naphthionic corrosive. it has a sensitivity to acids, thus had a restricted use to a corrosive pointer. The majority of the benzidine base direct colors have been kept away from because of its wellbeing risky nature.



**Figure 1.5 Direct Red 28**

**4,4-diaminobenzanilide substitute benzidine in C.I. Coordinate Black 166.**



**Figure 1.6 Direct Black 166**

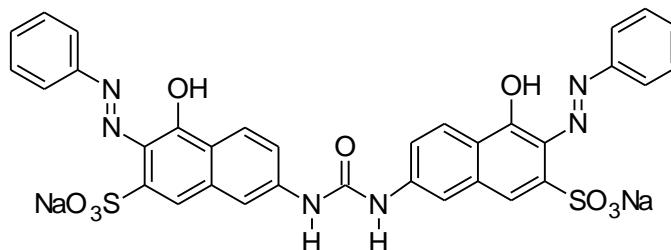
### **1.1.3 Photo-chromism of Direct Dyeing**

Colors, for example, sulphonated copper phthalocyanines, experience a photograph chromic minor departure from the cellulosic strands. The shade changes from turquoise to violet/ruddy blue, when it is presented to daylight for longer era. The procedure returns relentlessly, on expulsion from light. This can be improved either by the color settling operators or wrinkle oppose completes, subject to the capacity of material. The degree to which photograph chromic change happen, is connected with the force of the light and climatic dampness.

### **1.1.4 Augmentation of Direct Dyes in Solution**

Normally colors exists as amassed particle or atoms in watery arrangement as opposed to as individual particles. Color increases are having relatively shapeless structure with circulation of zones of various extremity that can promptly oblige more atoms. With the expansion in relative sub-atomic mass to ionic gathering the advancement of collection additionally increments, as in sulphonated anionic colors, the identical mass per sulphonic corrosive substituent is higher. Multi-sulphonated color anions settles as dimmers, where the 2 segments get situated in a planar course of action with the sulpho bunches joined at inverse end. At to begin with, dimers are framed, last lamellar micelles in which the units are situated lick pack of cards, is shaped because of expansion of anions. Sulphonated phthalocyanines sort planar chromophores have a tendency to experience such stacking. The normal of the aggregate number of atoms or particles per every total in alluded as conglomeration number. For direct colors, the conglomeration number is computed in its answer frame, which is observed to be diverse with the adjustment in the strategy for computation. As indicated by scientists, distinctive sizes of totals exist in arrangements. By the procedure of adsorption, comparative conveyance of whole total is saved by the separate of massive totals. If there should be an occurrence of direct colors, the level of total abatements with an expanding temperature. It increments with an expansion in the centralization of electrolytes. Albeit, a few direct colors are very much totaled at room temperature, however amid heating up, the degree of collection is unimportant in standard conditions, within the sight of an electrolyte.

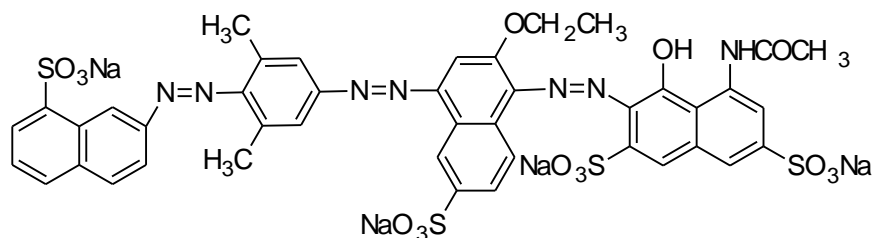
The quantitative simultaneousness between the total numbers assessed by various systems of estimation is slightest; therefore, the conclusions might be deducted from these outcomes, considering the relative patterns of total of various color structures. Under same temperature and electrolyte fixation, the C.I. Coordinate Orange 26 is exceedingly amassed as contrast with C.I. Coordinate Yellow 12.



**Figure 1.7 Direct Orange 26**

### 1.1.5 Decay of direct dyes

In the event that an Direct Dyesing is too much delayed, a slight disintegration of color may happen. The level of disintegration is quick in color shower then connected on the fiber which can be seen as a variety in shading. This may happen if the color is connected at temperatures over the bubbling temperature. This is because of the diminishment of the azo-linkages. This can be balanced out by buffering with ammonium sulfate. Oxidation with sodium m-nitrobenzenesulphonate and potassium chlorate or dichromate, can be useful if utilized circumspectly. Direct Dyeswith exposed azo-gatherings, are transcendently inclined to disintegration, i.e. C.I. Coordinate Yellow 12. In the C.I. Coordinate Green 33, the most uncovered of the 3 azo-gatherings is the separated focal linkage.



**Figure 1.8 Direct Green 33**

Colors containing azo-bunches bound by o,o`-substituents, uniquely o-sulphonate, are genuinely impervious to breakdown through coloring process.



## 1.2 Functional mechanism of direct dyes

Direct Dyes might be connected to cellulosic strands along with electrolyte, around the bubbling temperature.

Dynamics which drives their conduct are;

1. When submerged in an Direct Dyes, the cellulosic strands ingest color until equilibrium is accomplished, where a large portion of the color is taken up by the filaments.
2. The rate at which the equilibrium is achieved is alluded as the rate of dyeing. It varies for various dyes.
3. At equilibrium, the dye shower may debilitate which might be because of the substantivity proportion.
4. Exhaustion at balance decides of the substantivity of dye.

In the diminishing procedure, the main stage is alluded as strike in which the cellulosic filaments takes-up the dye on its surface. In the second stage, the dissemination of dye atoms into the fiber happens, to accomplish a balance appropriation. Add up to access into the center of the fiber is important to accomplish the required shade and speed. Time and temperature of dyeing are a portion of the essential flow that influence the assimilation of direct dyes on cellulosic filaments; different variables are dissolvability, conglomeration conduct, Liquor Ratio and salt convergence of individual dyes. A nitty gritty review by a SDC board of trustees demonstrated that the accompanying four factors were critical in characterizing the coloring properties and similarity of direct colors.

1. Movement or leveling power
2. Salt variability
3. Temperature variation on depletion

4. Depletion may be effected by liquor-ratio

**On SDC council suggestion, the Direct Dyes are be segregated as;**

- Class,-A: Dyes that have the property of 'self leveling'.
- Class-B: Dyes which doesn't have self leveling ability, but rather are controllable by the salt fixation. These are termed as "salt dependent".
- Class-C: Dyes which doesn't have self-leveling ability and are likewise touchy to salt focus , however salt fixation is by all account not the only controlling component, so temperature direction is additionally required. Thus, are referred as "temperature controllable".

## **1.3 Dye-bath variables**

The essential parameters, influencing the retention of direct colors by cellulose, from fluid arrangements are as per the following;

### **1.3.1 Temperature**

Strike and additionally fiber entrance are administered by the temperature at which color is connected. It enhances with rise in temperature. To achieve better nature of coloring in shorter time, the procedure is completed over the bubbling temperature. For a foreordained coloring time there is an ideal temperature at which color assimilation is at its most extreme.

### **1.3.2 Time of coloring**

With the expansion in coloring time, the level of infiltration additionally increments. Be that as it may, the drawn out coloring may likewise brings about the breakdown of direct colors.

### **1.3.3 Liquor Ratio**

Considerable changes in Liquor Ratio are applicable in coloring either cotton, thick or other cellulosic filaments.

### 1.3.4 Dye solubility

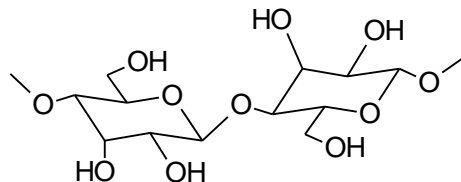
Colors with fine solvency are favored for coloring, especially at the lesser temperature and Liquor-Ratios, which are fundamental in cushioning forms.

### 1.3.5 Salt controllability

Salt-controlability is alluded as measure of direct-dyes that are influenced as the expansion of “electrolytes” changes in the dye bath. Direct dye change significantly with the impact of “electrolytes”. The electrolytes utilized are chiefly the Glauber's salt (sodium sulfate) and normal salt (“sodium chloride”). “Glauber's salt” can bring about precipitation of calcium sulfate on the colored material.

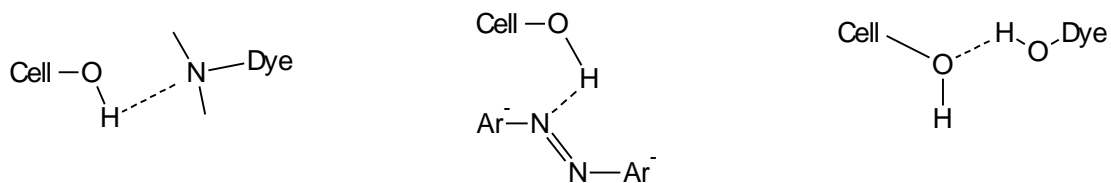
## 1.4 Dye fixation on fiber

Cellulosic strands are those regular filaments which are gotten from plant sources, e.g. cotton, material, thick, jute, hemp and flax. Cotton is practically unadulterated cellulose (i.e. 95%). Cellulose is a poly-saccharide having high sub-atomic weight polymer, that comprise of long chains of rehashing glucose units, with practically around 1300 units in a solitary particle. Because of an open structure, the cellulose particle is can oblige enormous color atoms, keeping in mind the end goal to encourage the entrance into the fiber. The cellulose atom is polar because of habitations of –OH gatherings in glucose units. This is an imperative character which encourage coloring. Bigger number of use classes of colors can be utilized for the coloring of cellulosic filaments, for example, sulfur, coordinate, vat, azoic and responsive colors (CHRISTIE, 2001).



**Figure 1.9 Structure of Cellulose**

- SO<sub>3</sub>Na bunches show in the Direct Dyes, making it water-solvent. Their interface with cellulose chains is hydrogen holding and dipole-dipole interaction, which are weaker strengths, which are in charge of low quickness, as illustrated in Fig.



**Figure 1.10 “H- bonding between cellulose and polar group in direct dye molecule”**

## **1.5 Anticipated research work**

Because of substantivity, the Direct Dyes get slackly connected with the fiber's atoms. This is because of the weak of Van der Waals forces and hydrogen bonding. The extent of this work is to integrate Di-J-Acid Urea-based direct colors to show signs of improvement in fastness of Dyeing. The resultant color will contain two azo-groups, in request to guarantee the high light fastness of the direct dyes.

## **1.6 Aims and objectives of research**

With a specific end goal to build fastness of direct dyes, the fuse of various non dangerous aromatic amines and Di J Acid Urea might be useful, in which every color contains two chromogens, every chromogen will deliver its own shading to give aggregate impact of chromogens to give new, extraordinary and splendid shading in a solitary dye.

## 2 Review of Literature

J. Szadowski, Z. Niewiadomski (1998) coupled J-corrosive and g-corrosive with toluene isocyanate parts, containing 02 Nos. of urea groups, having comparable properties to the known J-corrosive urea. The di-urea colors got from new intermediates indicate comparative properties to ordinary phosgenated coordinate colors.

NAVARRO AND SANZ (1999) investigated the variety in conglomeration of C.I. coordinate red color atoms in watery arrangement by changing the convergence of color temperature and arrangement of pH. Ideal conditions and color structure were assessed for coloring. Sub-atomic total was investigated by electrochemical and VIS spectro-photo metrical techniques. Decrease strategy utilized for electro chemical computations to color, outcomes were contrasted and previous research of different creators given pH and various centralization arrangement. It was observed that pH impact dyeing.

BELLO (2000) orchestrated 5,10-dihydrophenophosphazine based direct colors, containing disazo-bunch, which were employed for the benzidine substitution containing disazo-aggregate. Cotton texture was colored with these recently incorporated colors that delivered purple to blue shades. Particle electrospray mass spectrometry was utilized to affirm color structure.

WOJCIECHOWSKI et al., (2003-a) concentrated the blend of symmetric, direct colors. Cotton was than dyed with it to concentrate its properties. Spectro-photometric properties were likewise inspected which showed that the disazo colors have a solid propensity towards accumulation in arrangement furthermore on the substrate, which was affirmed by the reduction spectra. . B1 and B8 were used by leveling specialist.

WOJCIECHOWSKI et al., (2003-b) blended benzidine free direct colors. Integrated colors were secondary amide of iso-and terephthalic acids and J-acids. Cotton fiber was dyed to conclude the spectro-photometric properties.

SIMU et al., (2004) incorporated another symmetric disazo coordinate color as the center segment. Salicylic corrosive was utilized as the coupling part.

YAN et al. (2005) made 4,4-Diaminodiphenylurea, which was utilized instead of benzidine colors.

WOJCIECHOWSK (2005) incorporated direct colors so as to concentrate the substantivity and spatial structure of dissolvable polycyclic colors for coloring cellulose filaments.

SOCHA (2006) examined the electrochemical behavior of C.I. Red 81 and C.I. Black 36 arrangements by utilizing Pb and Hg anodes.

FEIZ. (2007) synthesized direct dyes by utilizing syn-tans and a syn-tan/cationic framework to color fleece and nylon-6 to study the effect of after treatment.

HANNA (2007) incorporated direct colors instead of benzidine dyes. Dis-aryl hydrazono sulfur-containing direct dyes were incorporated.

JIN-SEOK AND FREEMAN (2007) utilized *Daphnia magna* to assess amphibian poisonous quality of direct colors.

REN ., (2007) worked on direct blue color epitomized meso-structured MCM-41 composites and found it verity of optical applications.

SALEEM , (2007) checked the absorption of violet 17 and direct red-80 azo-colors from arrangement on cotton fiber.

KUO., (2008) concentrated on adsorption of direct dye via carbon nano-tubes furthermore evaluated its stability, energy and thermodynamics.

MARIA. (2009) manufactured di-azo colors containing 4 -4 diaminostilbene 2-2 disulfonic acid as pivotal part.

“BURKINSHAW, KUMAR” (2010) checked the impact of “polyvinyl as after-treatment” of coordinate colors on cotton.

CHEN., (2010) investigated the impact of multi anionic detergents and their connection with direct colors. In 2011 he studied bio-sorption of Direct Red-31 and Direct Orange-26 colors by rice husk

Some other efforts in this regard, may be summarized as follows;

Scientists	Year	Study
“SAFA, BHATTI”	2011	Investigate bio-sorption of Direct-dye Red,31 and Direct dye Orange,26 colors on rice husk material
“WANG, YAN”	2011	Investigated the adsorption expulsion of direct yellow dye utilizing bamboo charcoals modified with various chemicals
ZHAN et al.	2011	Investigates oxidation of direct blue azo-dye utilizing solvo-thermally incorporated copper hydroxide nitrate
Dinesh M. Patel	2011	proportioned bisazo–bisazo methane dispersed dye
B. Ahmad	2012	Synthesis of vinyl sulphon base dyes
Banu Babür, Nermin Ertan	2014	Synthesized monoazo dyes from ethyl,2-amino4-4-substitutedphenyl) thiophenes
Mingbo Ma and Munir Hussain	2015	shade of actually yellow-dyed silk
Hatem E. Gaffer , Moustafa M. G. Fouda	2015	novel naturally dynamic scatter dyes

**Table 2.1 Scientists Contributions**

Ghulam, Makshoof (2015) synthesized,characterized and afterward connected new arrangement of 4-amino-1-phenyl-5-pyrazolone based azo corrosive dyes.Multi chromic metal buildings of these colors 3d move metals Chromium, Iron and Copper were additionally expert. The structures of all recently blended mixes were affirmed by investigative information and spectroscopic procedures. The incorporated colors were connected on cowhide to evaluate their

light speed, wash quickness and rubbing speed and were appeared to have high estimations of 5-6, 4-5 and 4-5 separately by most extreme colors.

Nazia, Naeem, Fahad (2016) incorporated LaSmTiZrO<sub>7</sub> by means of smaller scale emulsion method, while SnSe and their composite by utilizing the aqueous approach took after by affirmation by XRD procedure. The combined synergist materials have then been utilized for the photocatalytic corruption of mono azo foron blue color under the unmistakable light illumination. The arrangement of vitality levels demonstrates that the electrons/gaps recombination can be minimized with the development of LaSmTiZrO<sub>7</sub>-SnSe composite. The photograph degradation results affirm that the composite has better effectiveness under obvious light illumination when contrasted with that of individual impetuses. The XRD examination after photograph debasement prepare affirm



## 3 Apparatus and Experimental Setup

### 3.1 Experimental Setup

All of the chemicals used in this study were obtained from Haric Dyestuff, Arzoo Textile, layallpur laboratories and Research and Development lab of NFC IEFR.

The synthesis of the dyes was carried out in Research & Development Lab of NFC Institute of Engineering and Fertilizer Research and Haric Dyestuff.

Synthesized dyes sample were sent to Government College University Faisalabad and National Textile University for analysis by UV-Visible spectrophotometer and FTIR respectively.

Bleached cotton sample was obtained from Jhang Fabrics Ltd Faisalabad. Wash-fastness, light-fastness, crock-fastness and Color coordinates data were investigated in jhang Fabrics Ltd Faisalabad. Colorimeter was used to find color coordinate data.

Chemicals and Apparatus used in this research are given below:

- 1 Sodium nitrite
- 2 C acid (2-amino-5-chloro-4-methyl benzene sulfonic acid)
- 3 Congo red dye
- 4 Ehrlich reagent
- 5 Na-Napthionate
- 6 Hydrochloric acid
- 7 Di-J-acid Urea
- 8 K acid (4-amino-5-hydroxynaphthalene-1,7-di sulfonic acid)
- 9 Para nitro Aniline (PNA)
- 10 Sodium carbonate
- 11 Sodium nitrite
- 12 Starch iodide paper
- 13 Sulfanilic acid
- 14 Sulfo Tobias Acid (STA)
- 15 Sulfamic acid
- 16 Potassium Chloride
- 17 pH Meter
- 18 Ice/Ice Bath
- 19 Vinyl sulphonate
- 20 Hot Plate /Magnetic Stirrer

- 21 Thermometer
- 22 Beakers
- 23 Experimental Setup

### 3.1.1 Synthesis of dyes

Following are the steps involved in the synthesis of desired dyes

- 1-Preparation of J Acid Urea Solution for coupling reaction (solution 1)
- 2-Diazotization reaction of different aromatic amines (solution 2)
- 3-Coupling reaction of solution 1 & 2 for dye preparation.

#### Preperation of samples and Experimental Setup

Samples obtained are dried and grinded to obtain accuracy in mixing and maximum conversions of reactions.

Samples of desired chemicals are calculated as per given data sheet from manufacturers to 100% purity.



**Figure 3.1 Experimental Setup**

The experimental setup was established in R & D lab of NFC IEFRR Faisalabad. The setup consists of Ice Baths followed by beakers containing pH meter prob. Thermometer in a fully isolated environment.

## DI-J-Acid Urea Solution

Freshly fine grinded powdered acid urea taken as per required stoichiometric ratio in coupling reaction with diazonium salt i.e (1 Di urea : 2 Diazonium salt) and available concentration to 100% purity basis and mix it with magnetic stirrer in a distilled water to make a solution. In order to neutralize the solution, powdered  $\text{Na}_2\text{CO}_3$  slowly added to the solution till pH became 7. Temperature is maintained at 0-5 °C.

### 3.1.1.1 Diazotization

Diazonium compound is prepared by the reaction of **aromatic amines** with  $\text{HNO}_2$  prepared in situ with  $\text{HCl}$  and  $\text{NaNO}_2$  and slow stirring. The reaction is carried out at 0~5 °C in a fully isolated ice bath. The pH is maintained at 2 in order to avoid the  $\text{N}_2$  formation favoured by low pH by using 18% w/v  $\text{Na}_2\text{CO}_3$  and reaction was continued for 01 hr with continuous slow magnetic stirring and controlled temperature at 0~5 °C. Potassium iodide paper for confirmation of acidic solution. At the end Sulfamic acid is poured to neutralize excess  $\text{HNO}_2$ .

### 3.1.1.2 Coupling Reaction

Reaction of diazonium compound and some organic aromatic compound resulted in coupling reaction at controlled conditions. It is an electrophilic substitution reaction in which diazonium salt is electron loving and arene is neutron loving. Example given below. There are multiple mechanisms introduced like base catalyzed reaction of Phenol reacts with benzenediazonium chloride to produce yellowish orange dye

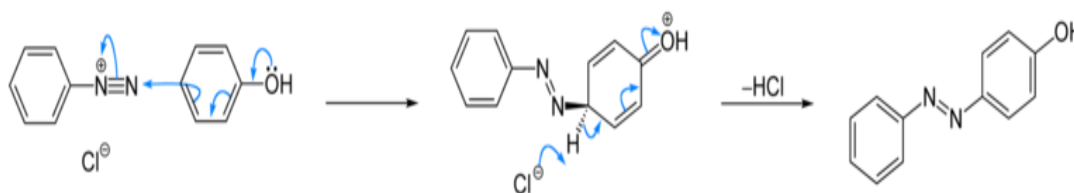


Figure 3.2 Coupling reaction

### 3.1.1.3 Coupling Reaction for preparation of J-Acid Urea dyes

Di-J Acid based direct dyes will be prepared using following aromatic amines

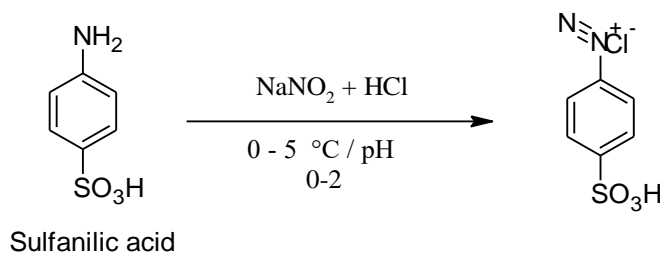
- 1- Sulfanilic acid

- 2- Aniline
- 3- Sulfo tobias acid
- 4- C-acid
- 5- K-acid
- 6- Sodium Napthanate
- 7- Vinyl sulphonate
- 8- Para-nitro-aniline

The synthesis is a straight forward conventional and economical method which consist of diazotiation followed by coupling. The effect of the molecular structure of the dyes on their colour and affinity for cellulose fibres will be studied. As far as environmental aspects are concerned which are the key issues now a days. The traditional spectroscopic characterization of the produced dyes will be done with F.T.I.R and to check projected dye structures

### 3.1.1.4 Diazotization of Sulfanilic Acid

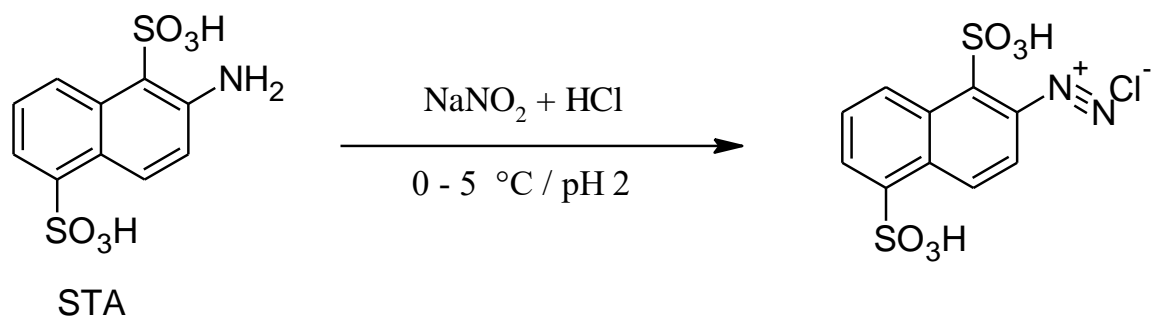
Sulfanilic acid (10.4g, 0.06mol on 100% basis) was mixed with deionised water (50 ml and stirring), conc. HCl (13.2 ml) and ice. The temperature of reaction mixture drop to 0~5 °C and then NaNO<sub>2</sub> (4.5 g, 0.01 mol) dissolve in distilled water (10 ml) was poured dropwise to prepare “diazonium salt”. The solution was then agitated for 01 hour. While mixing, excess HCl and HNO<sub>2</sub> was checked by the appearance of blue color on congo red paper and blackish color on starch iodide paper respectively.sulfamic acid is added for Excess HNO<sub>2</sub> to be decayed. At the end solution was neutralized by using 18% w/v Na<sub>2</sub>CO<sub>3</sub>.



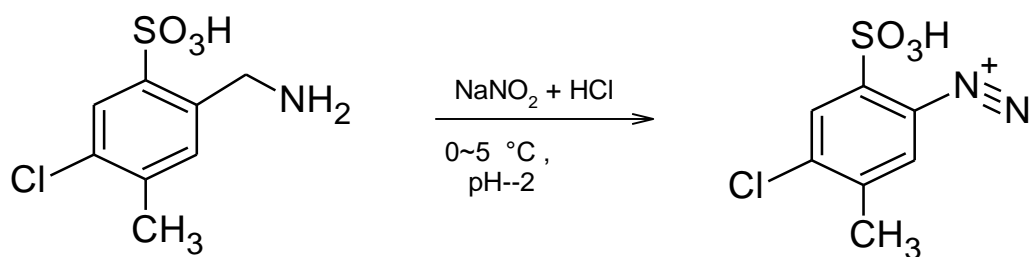
**Figure 3.3 Diazotization Reaction of Sulfanilic Acid**

Similarly Aniline (5.58 g, 0.06 M), K-acid(19.15 g,0.06 M), C-acid STA (21.1 g, 0.06 M), sodium-naphthonate (3.25g, 0.01mol), anthranilic-acid (1.40g, 0.01mol), K-acid (5.45g, 0.01mol) were used to yield the consequent “diazonium-salt solutions”. Chemical structures of different diazonium salts are given in Table 3.1.

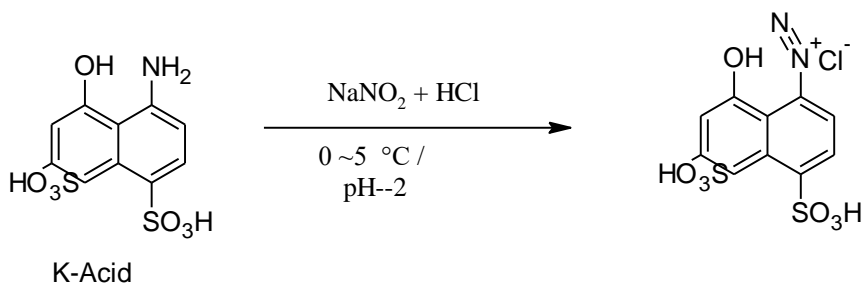
Diazotization of sulfotobias acid



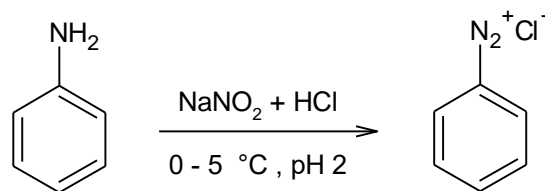
**Figure 3.4 Diazotization Reaction of STA**



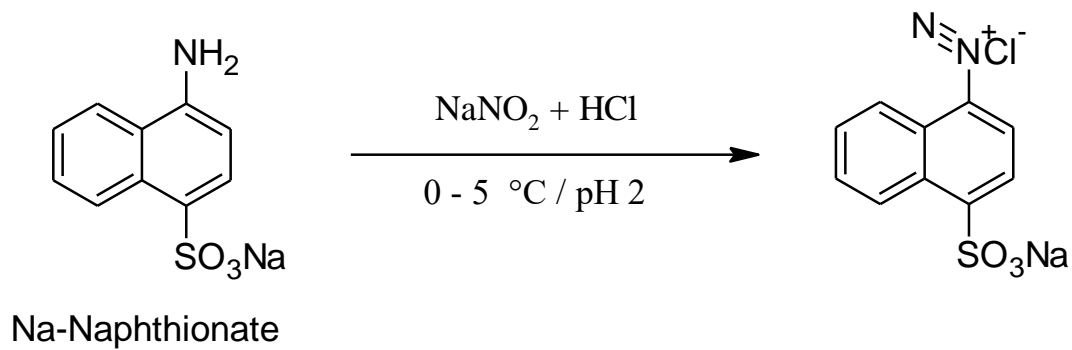
**Figure 3.5 “Diazotization Reaction of C-Acid”**



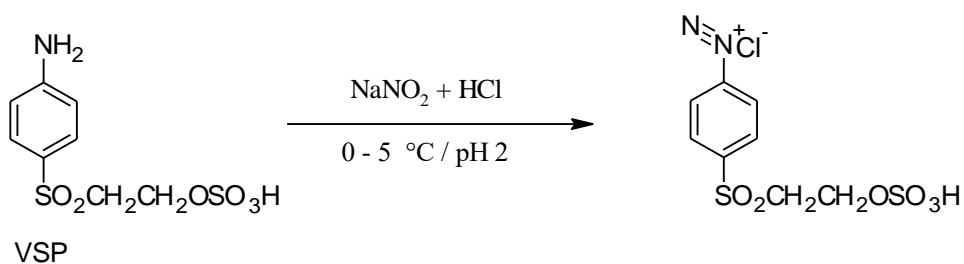
**Figure 3.6 “Diazotization Reaction of K-Acid”**



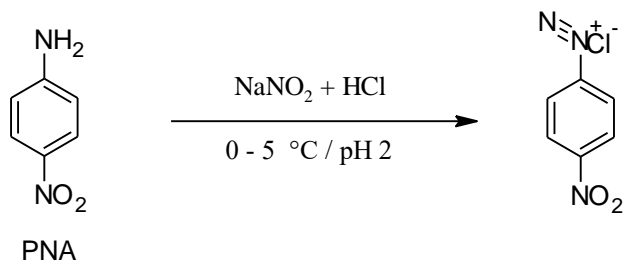
**Figure 3.6 “Diazotization of aniline”**



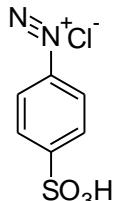
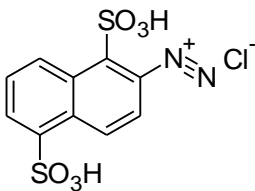
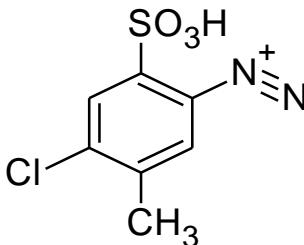
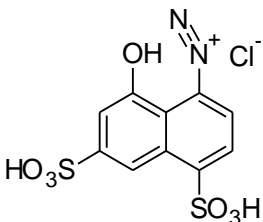
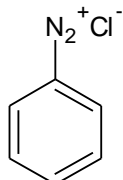
**Figure 3.7 “Diazotization Reaction of Sodium Naphthionate”**

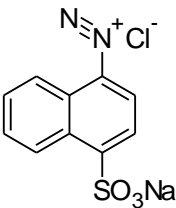
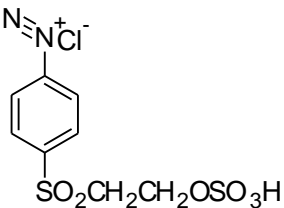
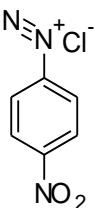


**Figure 3.8 “Diazotization Reaction of VSP”**



**Figure 3.9 “Diazotization Reaction of PNA”**

Diazonium Salt	Diazonium salt of	Structure of Diazonium Salt
1	Sulfanilic acid	
2	Sulfo Tobias Acid	
3	C-acid	
4	K-acid	
5	Aniline	

6	Na-Naphthionate	
7	Vinyl sulfone para ester	
8	Para nitro aniline	

**Table 3.1 Chemical structures of different Diazonium Salts**



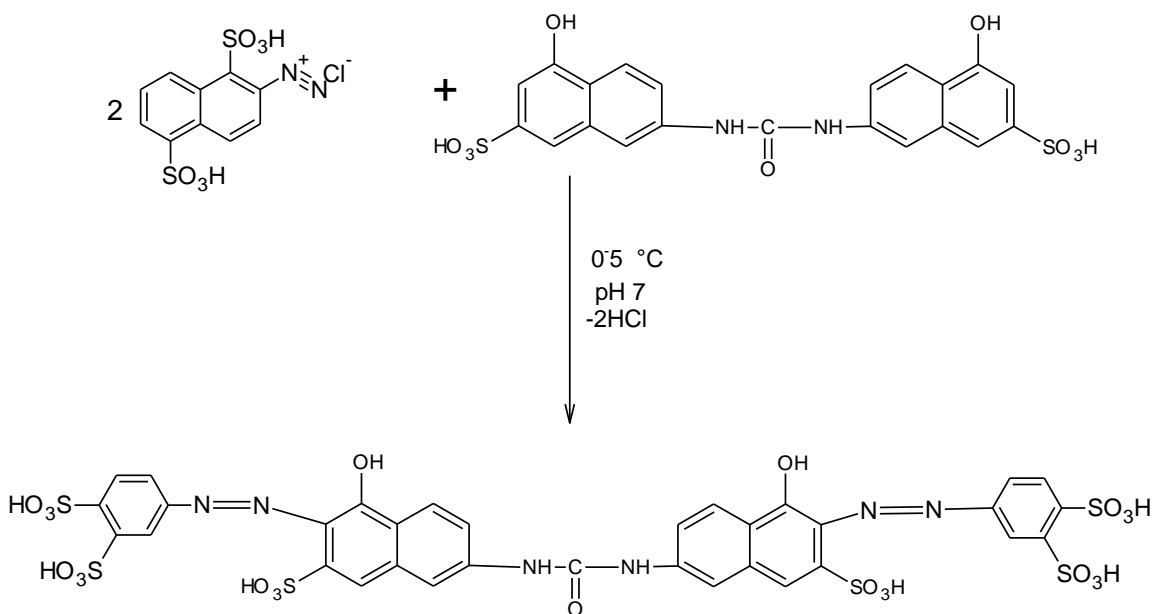
## 3.1.2 Coupling reactions

### 3.1.2.1 Chromogens based on H-acid

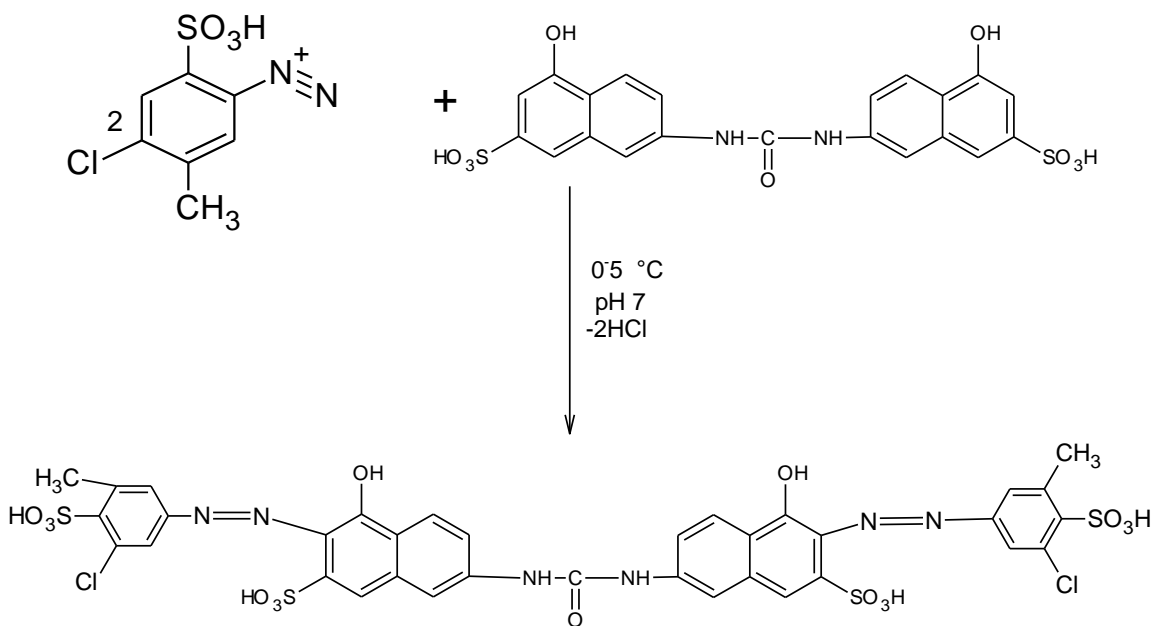
At start pH of solution was maintained at 7.5 by adding  $\text{Na}_2\text{CO}_3$ . Solution of H-acid (4.1g, 0.02mol) in water was prepared. While continuous stirring solutions of H-acid (0.02mol) and recently prepared diazonium salt solutions (0.02mol) the rate of 1 - 11 drop per minute. The pH of reaction was set at 7 by adding  $\text{Na}_2\text{CO}_3$  and the reaction was continued for 1 hour at temperature of 0-5 °C.

s

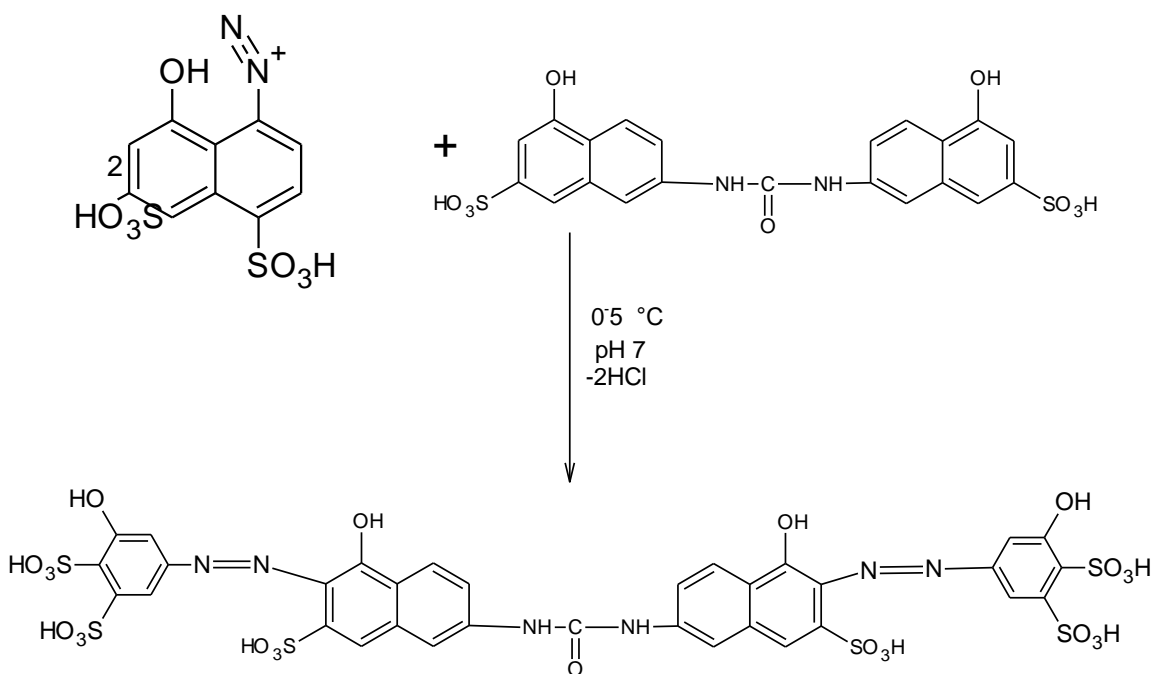
**Figure 3.10 “Reaction of Diazonium salt of Sulfanilic Acid and Di-J acid Urea”**



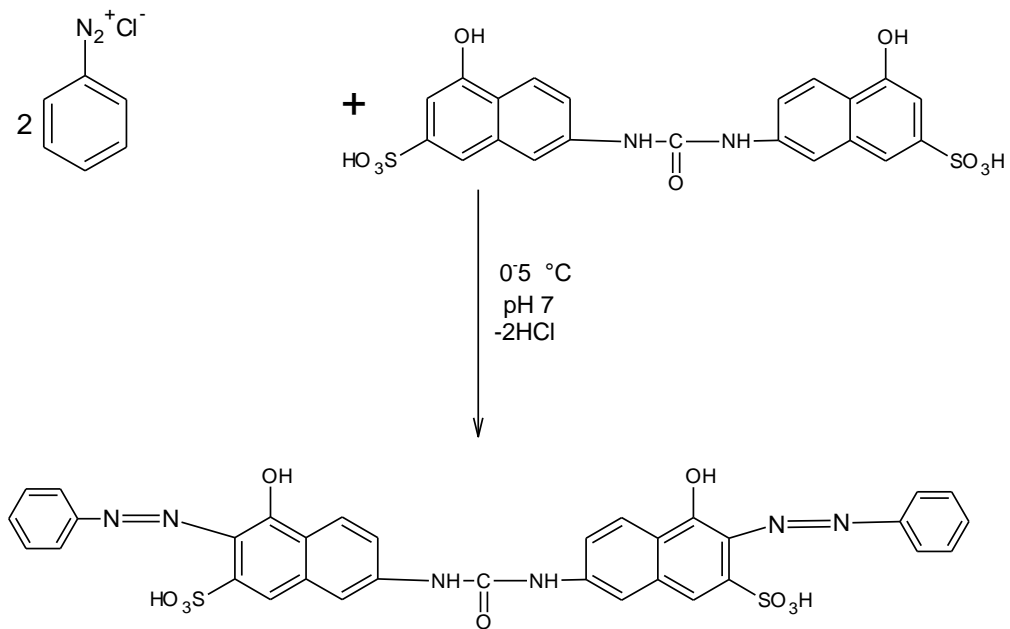
**Figure 3.11”Reaction of Diazonium salt of STA and Di-J acid Urea”**



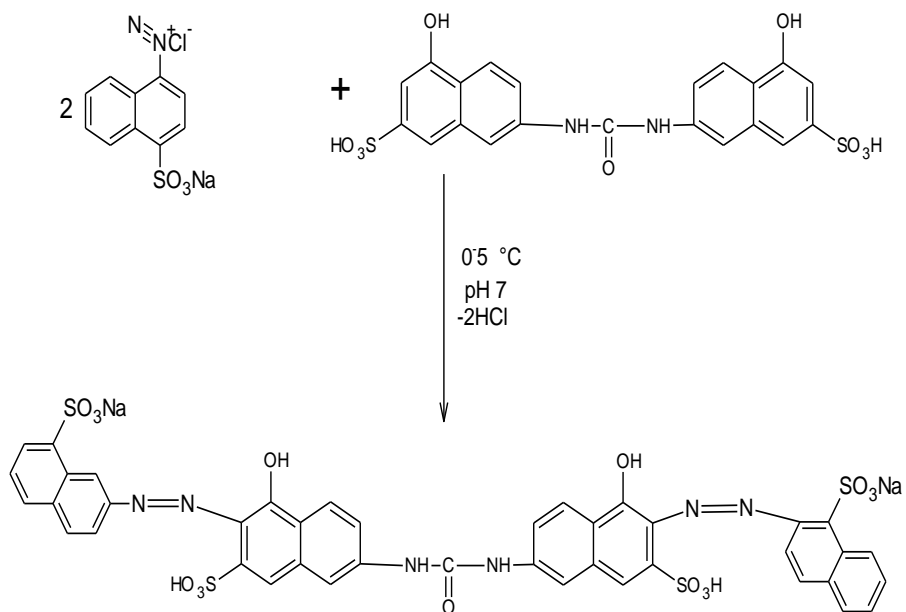
**Figure 3.12 “Reaction of Diazonium salt of C-Acid and Di-J acid Urea”**



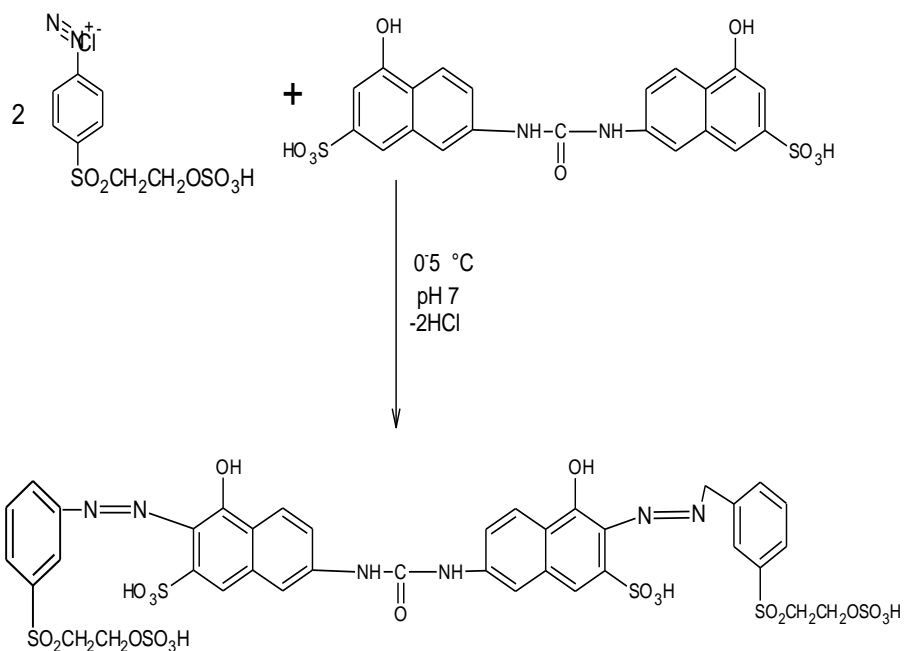
**Figure 3.13 “Reaction of Diazonium salt of K-Acid and Di-J acid Urea”**



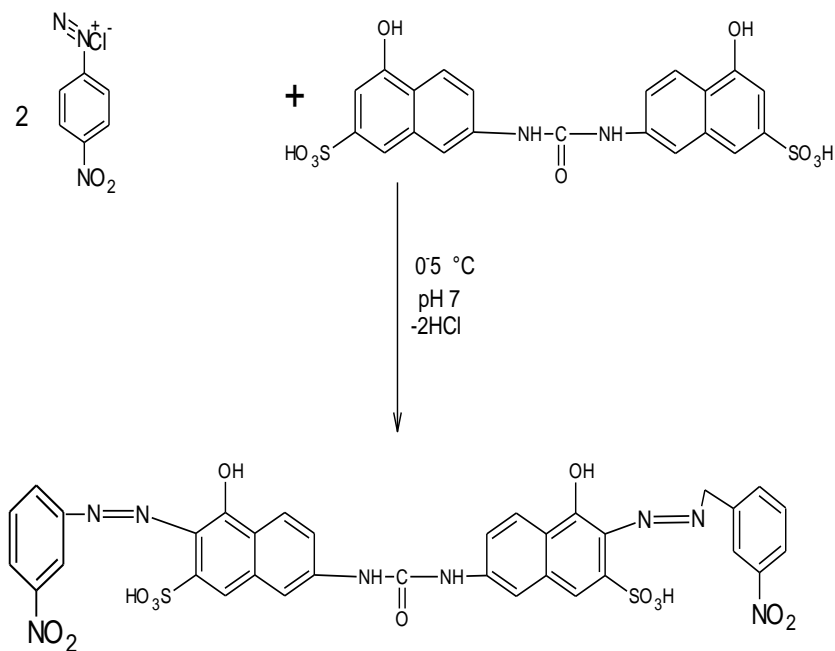
**Figure 3.14 “Reaction of Diazonium salt of Aniline and Di-J acid Urea”**



**Figure 3.15 “Reaction of Diazonium salt of Sodium-Naphthionate and Di-J acid Urea”**



**Figure 3.16 “Reaction of Diazonium salt of Vinyl Sulfone para ester and Di-J acid Urea”**



**Figure 3.17 “Reaction of Diazonium salt of Para-Nitrotoulene and Di-J acid Urea”**

Chromogen	Diazonium salt / Coupler	Structure of chromogen
1	Sulfanilic acid / Di-J-acid Urea	
2	Sulfo Tobias Acid/ Di-J-acid Urea	
3	C-acid/ Di-J-acid Urea	
4	K-acid/ Di-J-acid Urea	
5	Aniline/ Di-J-acid Urea	
6	Na-Naphthionate/ Di-J-acid Urea	
7	Vinyl sulfone para ester/ Di-J-acid Urea	
8	Para nitro aniline/ Di-J-acid Urea	

**Table 3.2 Chemicals Structures of Different Chromogens with Di J acid urea**

### **3.1.2.2 Visible absorption data**

The sample of dye solution were prepared by preparing a dye solution in deionised water. The absorption spectra obtained,  $\lambda_{\max}$  values were recorded with the help of Aquarius CE 7200 Spectrophotometer apparatus.

### **Fourier Transform Infrared Spectroscopy (F.T.I.R)**

Fourier Transform Infrared Spectroscopy some times called FTIR Analysis or FTIR Spectroscopy, is a technique used to identify functional groups of compounds. It uses infrared rays to analyze samples.

Adequate powder samples are usually prepared by shredding some material off of the sample that is thin enough to obtain a sharp spectrum.

#### **Following were the steps performed for FTIR Analysis**

- (i) Compilation of milieu spectra to take away from the test spectra in order to ensure the actual sample is that to be analyzed.
- (ii) Analysis for Absorption spectra showed the functional groups in peaks. Absorbed infrared rays of various wavelengths indicates different groups.
- (iii) The analytical spectrums obtained were then compared in reference literature spectra to identify components or to find a “best match” for unknown material using the literature spectra for known substances.

### **3.1.2.3 Dyeing procedure**

Fabric sample were dye in 2% dye solution and 20:1 ratio of dye liquor to fabric sample in hot water (at 30o C) for 05 min. grinded salt NaCl (15g) added and temperatre maintained at 30 oC for next 10 min. powder Na<sub>2</sub>CO<sub>3</sub> then added to solution while temperature increased to 80oC for 45 min. Sample then washed with hot water and rubed with 2 g/l soap at 01 hr for 05 min. Finally washed with hot and dried.

### **3.1.2.4 Colorimetric-data**

“L\* a\* b\*” figures of dyed sample were determined with the help of literature color data.

In which

L=Lightness, a=red color, -a=green color, b= yellow color, -b=blue color

### 3.1.3 Fastness tests

#### 3.1.3.1 Washingfastness test

As per ISO-105-CO1-1989 standard technique washing fastness checked, at following conditions.

Temperature	-	60 °C
Bath volume	-	100 ml
Time	-	30 min

To evaluate staining the 3''\*4'' size sample of dyed fabrics prepared. The change in color and stain checked by grey sclae. The scale from 1-5 indicates the results from lower to high quality.

#### 3.1.3.2 Lightfastness test

The standard of ISO 105-BO2:1989 used for lightfastness test under following conditions.

Light supply	Mercury
Panel-temperature	64 ± 1°C
Dry bulb temperature	44 ± 2°C
% Relative humidity	19 ± 5%
Duration	72 hours

Dyed fabric sample of size 2'\*3'' were exposed to light for 72 Hrs. The change in color and stain checked by grey scale. The scale from 1-5 indicates the results from lower to high quality.

#### 3.1.3.3 Crockfastness test

The standard of ISO 105-X12: 1989 test used for both dry and wet **Crockfastness by crock meter with 9N force to and fro**. The change in color and stain checked by grey scale. The scale from 1-5 indicates the results from lower to high quality.

## 4 RESULTS AND DISCUSSION

This Chapter deals with the concluding remarks of my thesis including the overall synthesis, test results and analysis of different Characterization techniques and Tests i.e Visible absorption spectrum, yield, fastness properties and Fourier Transform Infrared Spectroscopy (FTIR)

### 4.1 Percentage yield of dyes

Percentage yield of the dyes were calculated using the theoretical yield from limiting reaction of reaction and actual product obtained is given in table 4.1. Due to presence of impurities, salts produced during neutralization content of diazonium compound %yields are exceeding 100 percent, in true sense this situation is never possible.

$$\% \text{ Yield} = \frac{\text{Actual Yield}}{\text{Theoretical yield}} \times 100$$

Dye	Percentage yield %
1	126
2	122
3	130
4	119
5	150
6	136
7	115
8	106

**Table 4.1 Percentage yields of dyes**



## 4.2 Visible absorption data

This technique is used to study the variation in the absorbance of light over a range of wavelength.

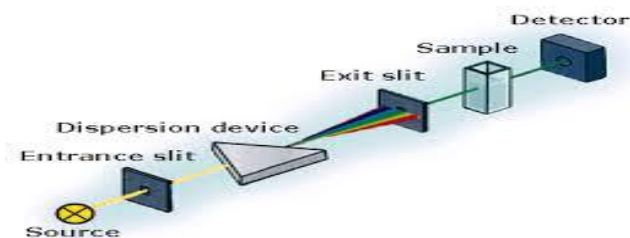


Figure 4.1 UV-Vis Mechanism

So, when exposed to light, the sample absorbs some of its wavelengths due on its chemical configuration and bonds. This transmission and absorption of light is evaluated by detectors, which monitors the reflected rays. The wavelength range is 200-1100nm. Upon light absorption, the electron, jumps from valance band to conduction band. The spectrometer scrutinizes that wavelength at which absorption occurs. Which than, plots a graph of the absorbance vs wavelength.

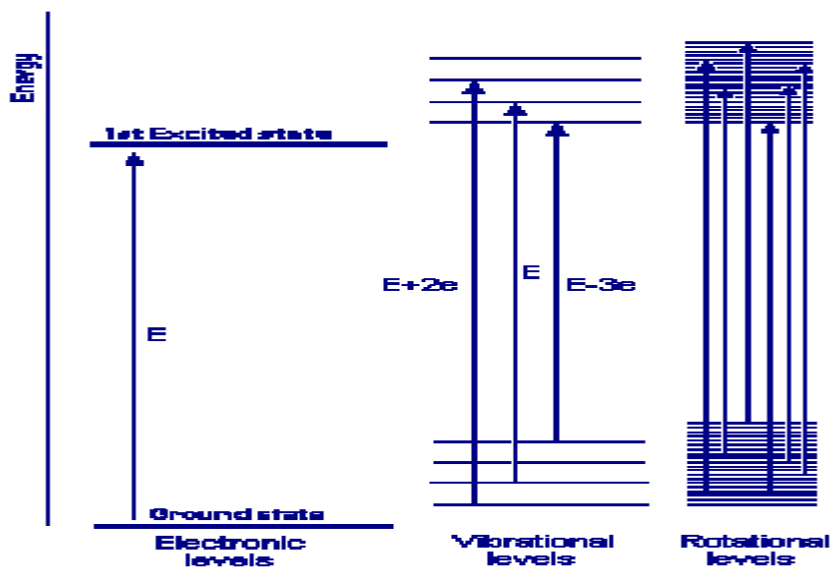


Figure 4.2 Molecules Energy Level

“Tauc equation” is used to find the bandgap, as;

$$\epsilon h\nu = (h\nu - E_g)^n$$

Here,

$\epsilon$  = Absorption,

$\nu$  = Frequency,

$h$  = Plank's constant,

$E_g$  = Band gap,

Where

$n = \frac{1}{2}$  for indirect band gap and

$n = 2$  for direct band gap

UV-Vis characterization was done with distilled water at 20°C and pH 7, to observe the visible absorption spectra of the synthesized dyes. Dyes # 1,2 and 7 showed two sharp peaks, due to presence in azo-hydrazone form and in conjugation with –OH group on H-acid, J-acid and 4NAP.

The absorption data ranges from 475nm - 574 nm, which falls in the region of yellow, green, blue, violet, red and orange.

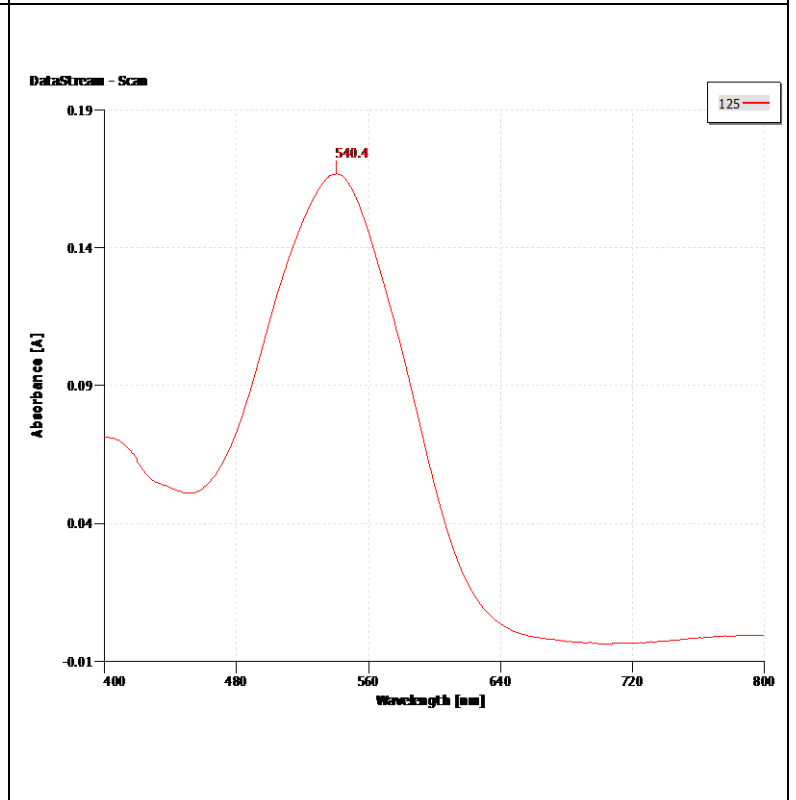
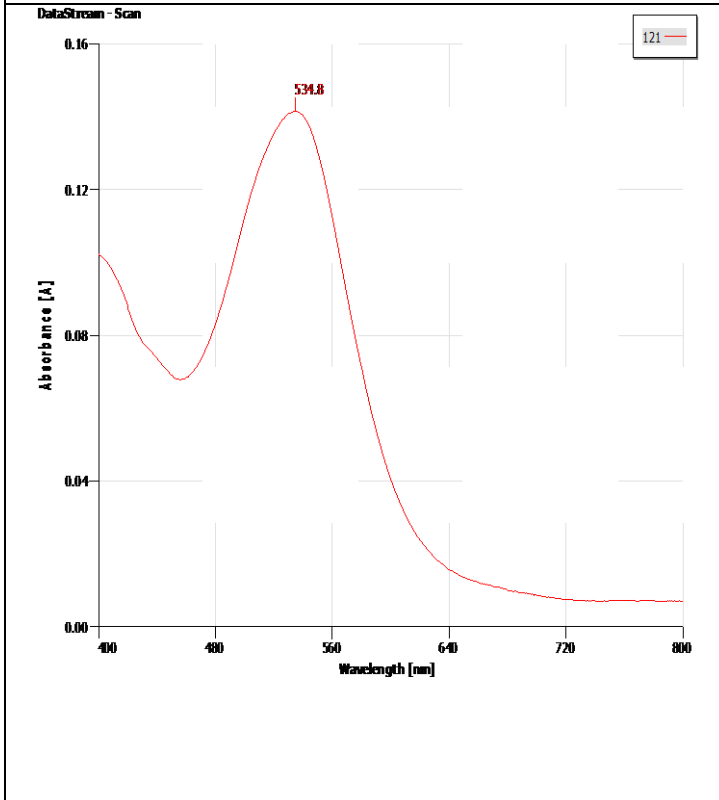
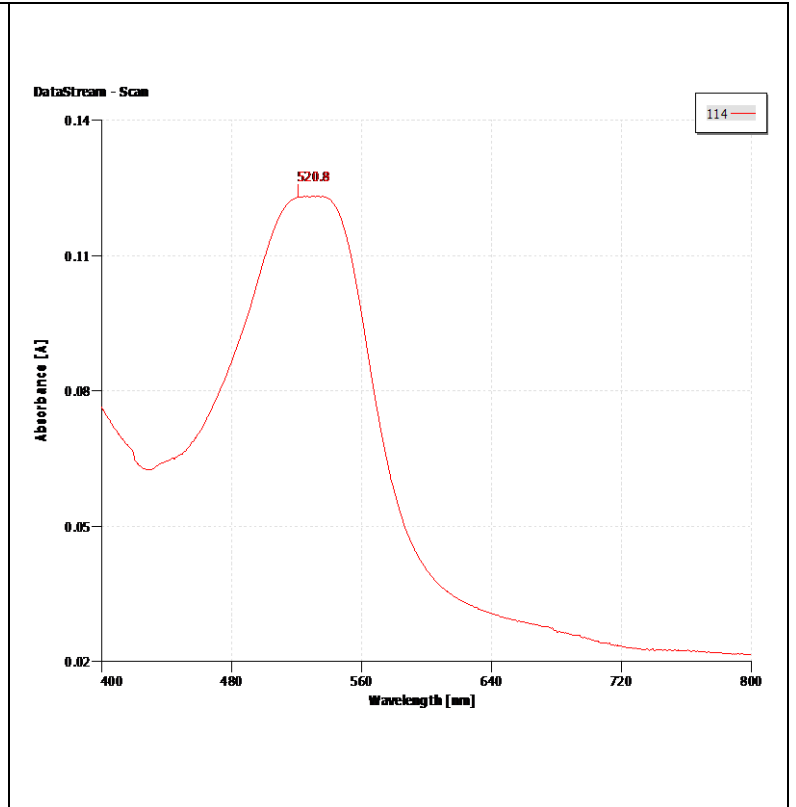
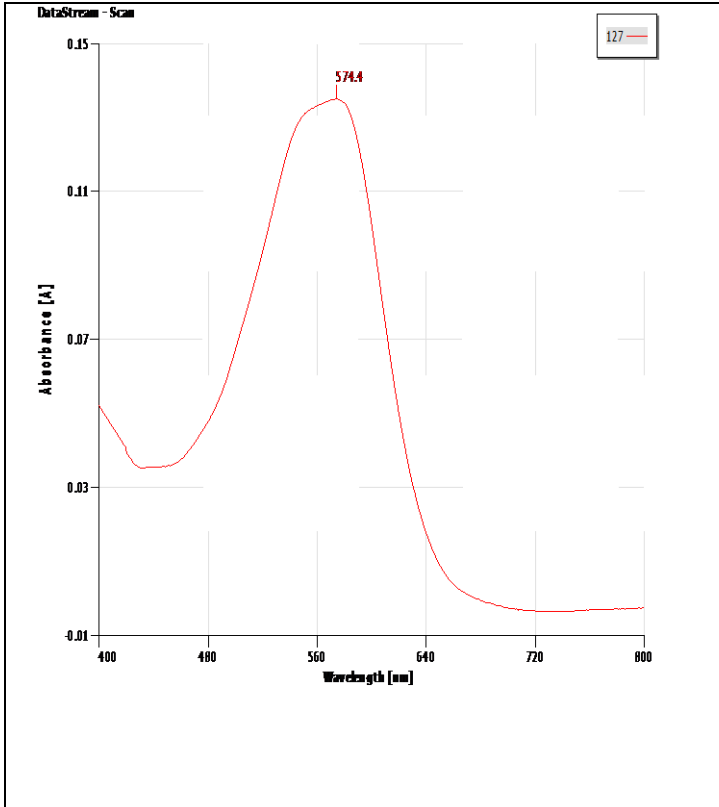
Chromogen	Diazonium salt / Coupler	Structure of chromogen
1	Sulfanilic acid / Di-J-acid Urea	
2	Sulfo Tobias Acid/ Di-J-acid Urea	
3	C-acid/ Di-J-acid Urea	

4	K-acid/ Di-J-acid Urea	
5	Aniline/ Di-J-acid Urea	
6	Na-Naphthionate/ Di-J-acid Urea	
7	Vinyl sulfone para ester/ Di-J-acid Urea	
8	Para nitro aniline/ Di-J-acid Urea	

**Table 4.2 Structures of dyes**

Dye	Colour	$\lambda_{\text{max}}$ (nm)
1	Redish/ violet	575
2	Bluish/ Pink	520.9
3	Yellowish/ green	534.9
4	Reddish/ grey	540.3
5	light yellow	480
6	Orange/ red	510.8
7	Pinkish	533.6
8	Greyish	475.7

**Table 4.3 Wavelength of dyes**



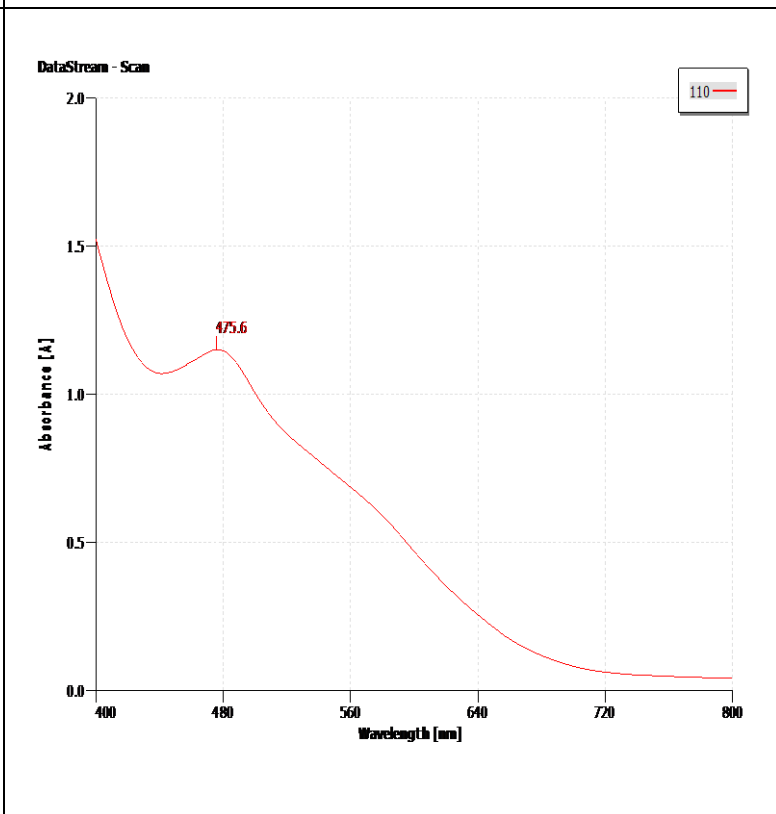
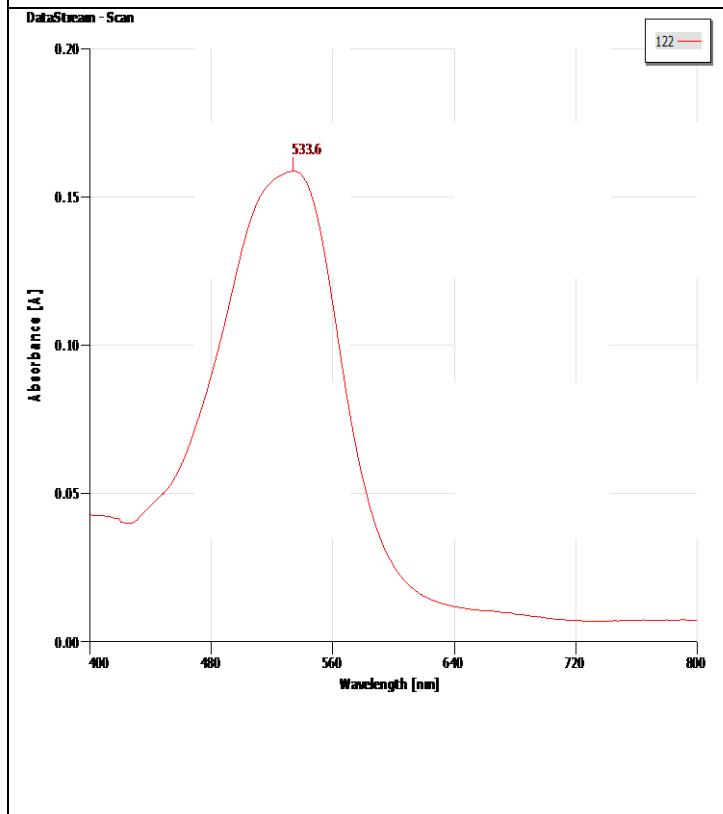
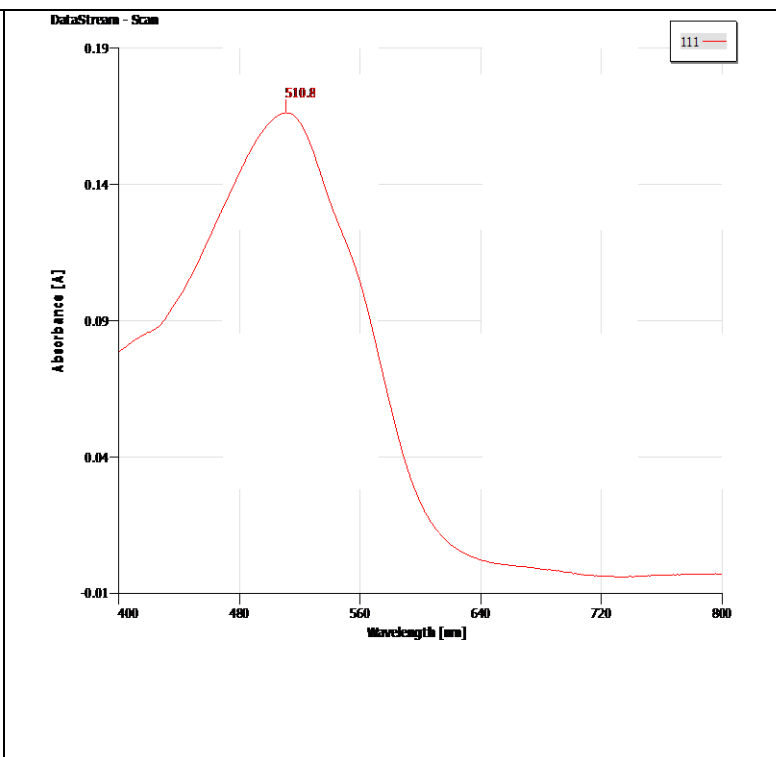
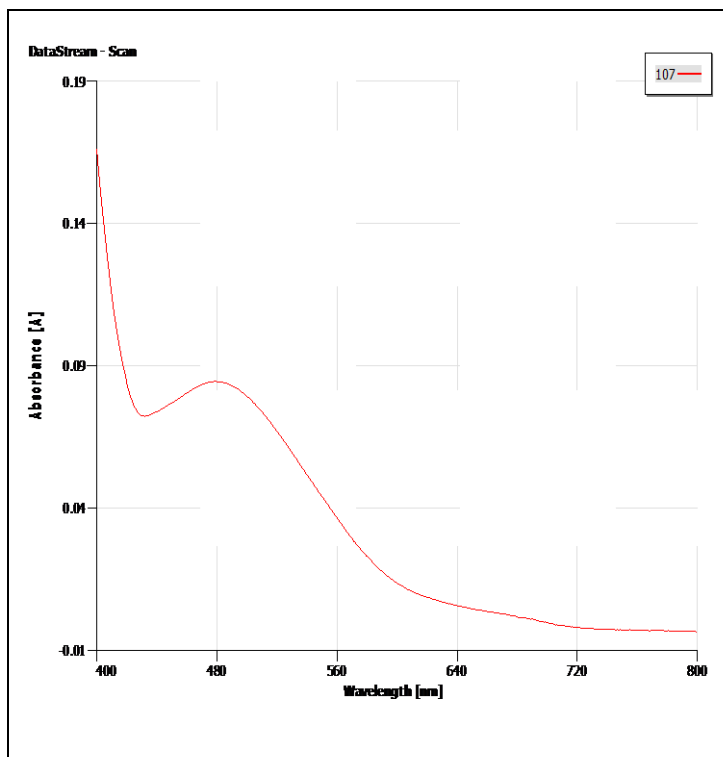


Table 4.4 UV-Vis Plots of Samples

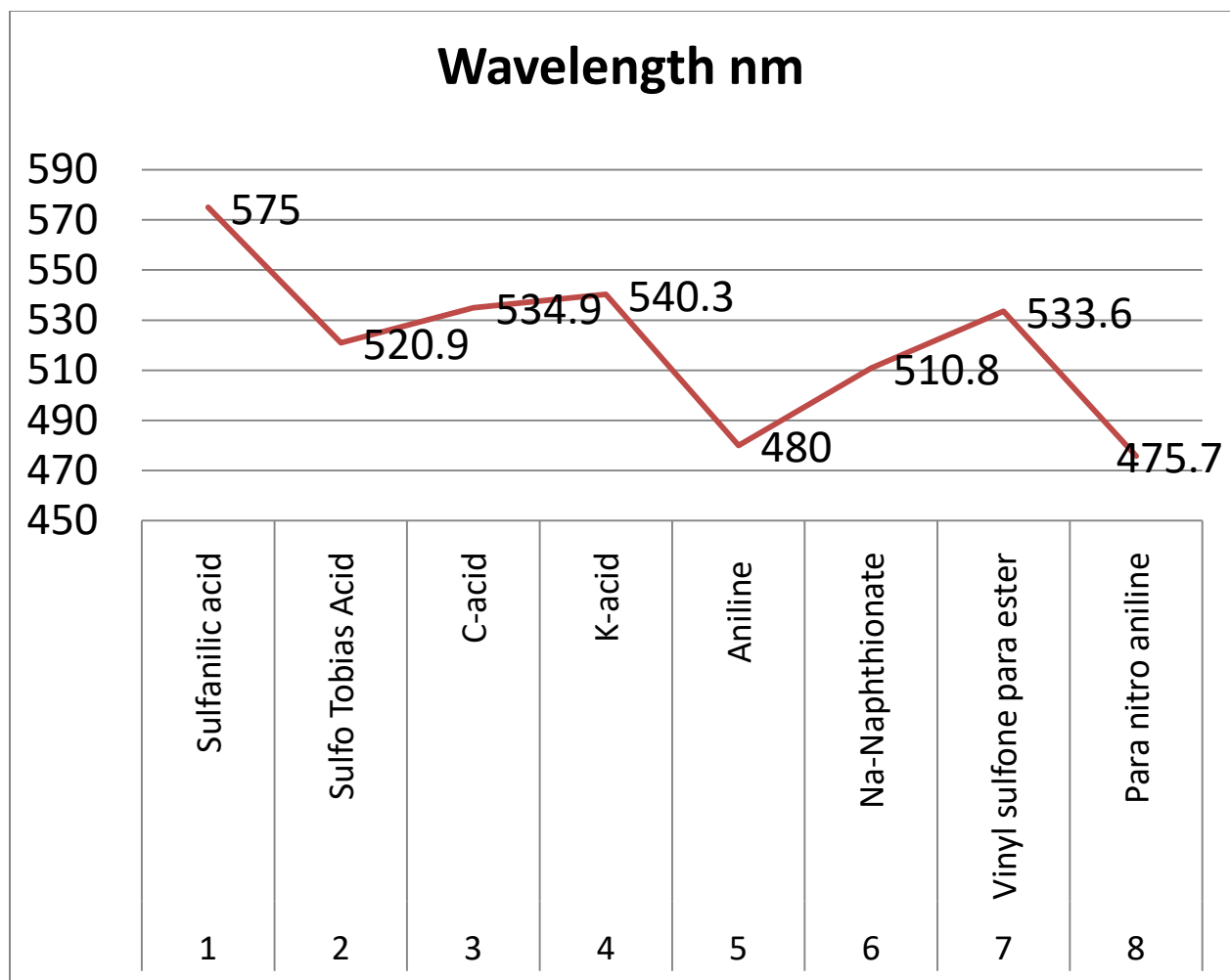


Figure 4.3 variation in wavelengths of dyes

### 4.3 Colorimetric data

Colorimetric data in lab color system for the dyed fabrics by exhaust dyeing method is given in table 4. In lab color system following are the nomenclature

**L\*** for brightness

**a\*** for red-greenish zone where + a\* exhibit red colour, and -a\* exhibit green color

**b\*** for yellow-blue shades in which + b\* exhibit yellow colour and - b\* exhibit bluish colour

**h\*** for Hue is measured anti clock wise ranging 0 ~ 360°

**C\*** for chroma which is perpendicular to **L\*** axis

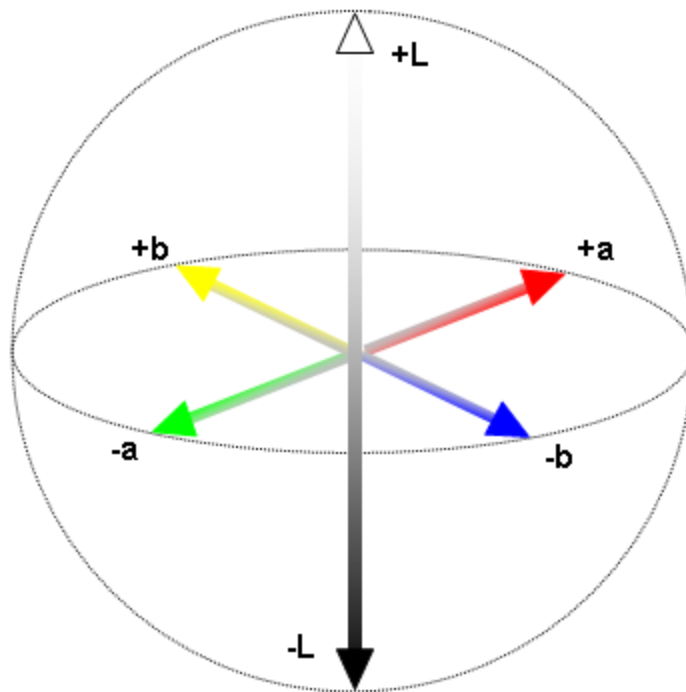
The resultant shades are given in figures and classified into color groups represented in tables.

First group represents pinks, ranging from 2 ~ 7 , their **a\*** values varies from 17 to 33 and **b\*** values from -2 to 9, indicating redder and slightly blue shades. Dye 2 exhibiting highest negative value of **b\*** value has higher amount of bluish color. Dye 6 exhibiting as violet from light violet to violet with lower **L\*** values and small **b\*** value of 1 exhibiting faintly yellow.

Dye 4 and 8 exhibiting gray shades with little deviation with low **C\*** values i.e 7 and 3 respectively shows grey scale.

Dye 5 indicates yellowish shade with **L\*** value 87, **a\*** value 2 and **b\*** value 5 showing the lighter yellow color .Dye 3. has **a\*** 2, **b\*** 7 and **L\*** 59 exhibiting dark yellowish shade and **C\*** value of 8 showing grey effect

Highest negative value of **b\*** is presented by Dye 2 i.e -9 exhibiting blue shade indicates that it is the mixture of red/yellow with blue.



Color coordinates

Dye	L*	a*	b*	C*	H
1	56.2	10.5	-1.08	10.5	354.2
2	55.3	30.03	-9.02	31.4	343.1
3	39.8	2.5	7.8	8.2	72.6
4	47.8	7.5	-0.8	7.5	253.5
5	57.7	2.18	5.1	5.5	57.1
6	54.7	24.6	1.4	24.6	3.3
7	78.1	28.3	-7.4	29.2	254.2
8	51.9	2.6	1.7	3.1	32.9

Table 4.5 Color coordinates data of dyes



<b>Groups</b>	<b>Dye</b>	<b>L*</b>	<b>a*</b>	<b>b*</b>	<b>C*</b>	<b>H</b>
Pink	2	65.31	30.04	-9.01	31.39	343.13
Red	7	68.14	28.29	-7.46	29.26	354.22
Light Violet	1	66.21	10.48	-1.07	10.54	354.16
Violet	6	54.76	24.63	1.44	24.67	3.36
Grey	4	47.82	7.50	-0.85	7.55	353.54
Yellow	5	87.69	2.17	5.11	5.55	67.04
Green	3	59.78	2.46	7.85	8.22	72.61
Brown	8	40.76	9.59	8.10	12.55	40.18

**Table 4.6 color coordinate data classified into color groups**

<b>Dye</b>	<b>L*</b>	<b>a*</b>	<b>b*</b>	<b>C*</b>	<b>H</b>
5	87.7	2.1	5.1	5.5	67.03
3	59.7	2.4	7.8	8.2	72.6
8	61.9	2.6	1.7	3.1	32.9
4	47.8	7.5	-0.8	7.5	353.5
1	66.2	10.4	-1.0	10.5	354.1
6	54.7	24.6	1.4	24.6	3.3
7	68.1	28.3	-7.4	29.2	354.2
2	65.3	30.0	-9.0	31.4	343.3

**Table 4.7 increasing trend of a\* values**

<b>Dye</b>	<b>L*</b>	<b>a*</b>	<b>b*</b>	<b>C*</b>	<b>H</b>
2	65.3	30.03	-9.02	31.4	343.1
7	68.1	28.3	-7.4	29.2	354.2
1	66.2	10.4	-1.0	10.5	354.1
4	47.8	7.5	-0.8	7.5	353.5
6	54.7	24.6	1.4	24.6	3.3
8	61.9	2.6	1.6	3.1	32.9
5	87.6	2.1	5.1	5.5	67.0
3	59.7	2.4	7.8	8.2	72.6

**Table 4.8 Increasing trend of b\* values**

<b>Dye</b>	<b>L*</b>	<b>a*</b>	<b>b*</b>	<b>C*</b>	<b>H</b>
4	47.8	7.5	-0.8	7.5	353.5
6	54.7	24.6	1.4	24.6	3.3
3	59.7	2.4	7.8	8.2	72.6
8	61.9	2.6	1.6	3.1	32.9
2	65.3	30.0	-9.0	31.3	343.1
1	66.2	10.4	-1.0	10.5	354.1
7	68.1	28.2	-7.4	29.2	354.2
5	87.6	2.1	5.1	5.5	67.0

**Table 4.9 Increasing trend of L\***

## **4.4 Fastness studies**

### **4.4.1 Washingfastness studies**

Fastness is a property used to determine the ability of a dye to retain on a fabric under different conditions. Washing fastness properties were checked and presented in a tabular form in table 4. The rating scale is ranges from 1-5 in which 1 represents (poor) and 5 represents (excellent).

<b>DYE</b>	<b>COLOR CHANGE</b>	<b>STAINING ON</b>		
		<b>Cotton</b>	<b>Nylon</b>	<b>Wool</b>
1	2	3	4-5	3-4
2	2-3	3-4	3-4	3-4
3	2-3	4	3-4	3-4

4	2-3	4	3-4	3-4
5	2-3	2-3	3-4	3-4
6	2-3	3-4	3-4	3-4
7	2-3	3-4	3-4	3-4
8	2-3	3-4	3-4	3-4

**Table 4.10 Washing fastness data of dyes**

#### **4.4.2 Lightfastness studies**

Light fastness properties were checked on dyed and printed fabric. In which fabric were exposed to mercury fluorescent for 72 hours under ISO 105-BO2:1989 standard. Due to better penetration and H-H bonds data shows moderate to good light fastness results.

DYE	COLOR CHANGE
1	4-5
2	5
3	3-4
4	4
5	3
6	4
7	3-4
8	4

**Table 4.11 Light-fastness data of dyes**

### 4.4.3 Crockfastness studies

Crock fastness was checked with the help of SDL Atlas, CM-5 crockmeter. In dry test excellent crockfastness rating were observed and good to very good results in wet test.

<b>Dye No.</b>	<b>Dry</b>	<b>Wet</b>
1	3~4	3~4
2	2~3	2~3
3	1~2	2~3
4	2~3	1~2
5	3~4	2~3
6	2~3	3~4
7	4~5	2~3
8	3~4	1~2

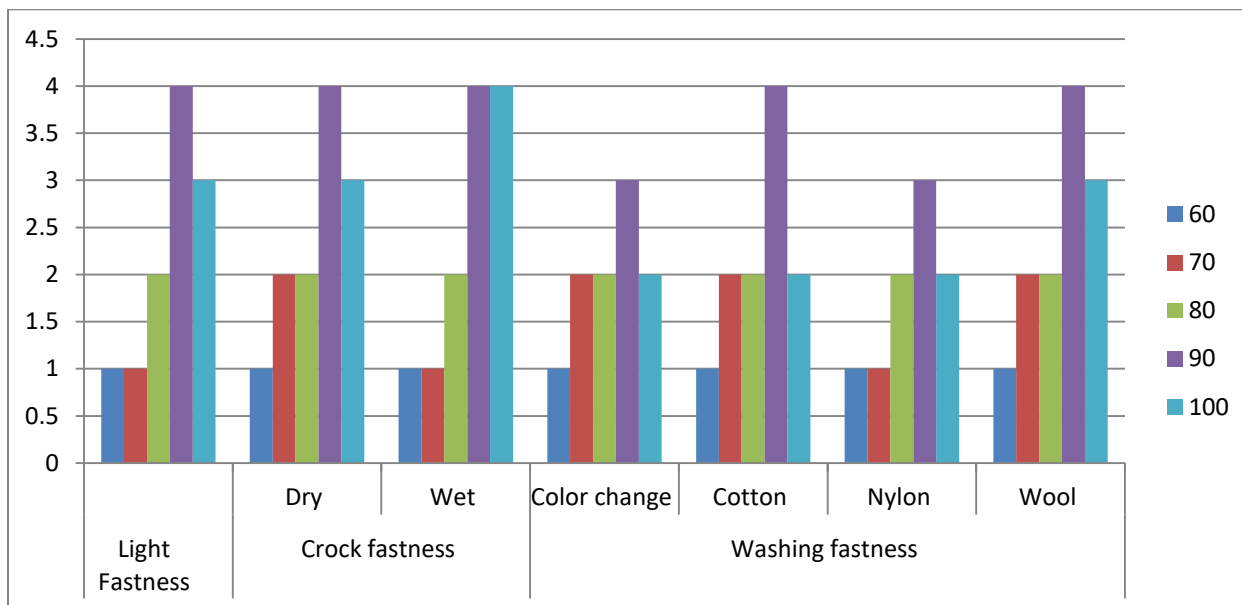
**Table 4.12 Crock-fastness data of dyes**

**4.4.4 Light Fastness, Crock Fastness, Washing Fastness Data at pH 7.0, LR60:1, Salt 10%, Time 30 min**

**Dye 1**

Sr No	Temperature °C	Light Fastness	Crock fastness		Washing fastness			
			Dry	Wet	Color change	Cotton	Nylon	Wool
1	60	1	2	1	1	2	1	1
2	70	2	3	2	2	2	2	2
3	80	3	3	2	2	2	2	2
4	90	4	3	4	3	3	3	3
5	100	3	4	3	3	3	3	2

**Table 4.13 Light Fastness-Crock Fastness-Washing Fastness Results of Dye 1**

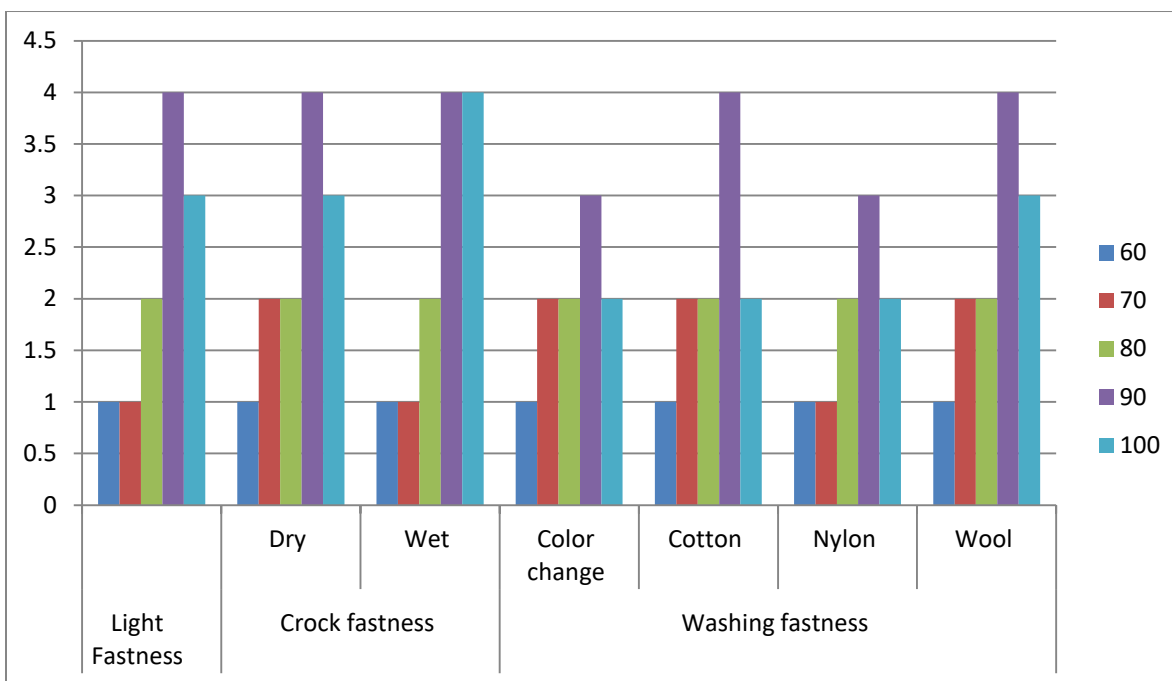


**Figure 4.4 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 1”**

**Dye-2**

Sr No	Temperature °C	Light Fastness	Crock fastness		Washing fastness			
			Dry	Wet	Color change	Cotton	Nylon	Wool
1	60	1	2	1	1	2	1	1
2	70	2	3	2	2	2	1	1
3	80	2	3	3	2	3	2	2
4	90	3	4	4	3	3	4	4
5	100	3	4	3	3	3	3	3

**Table 4.14 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 2”**

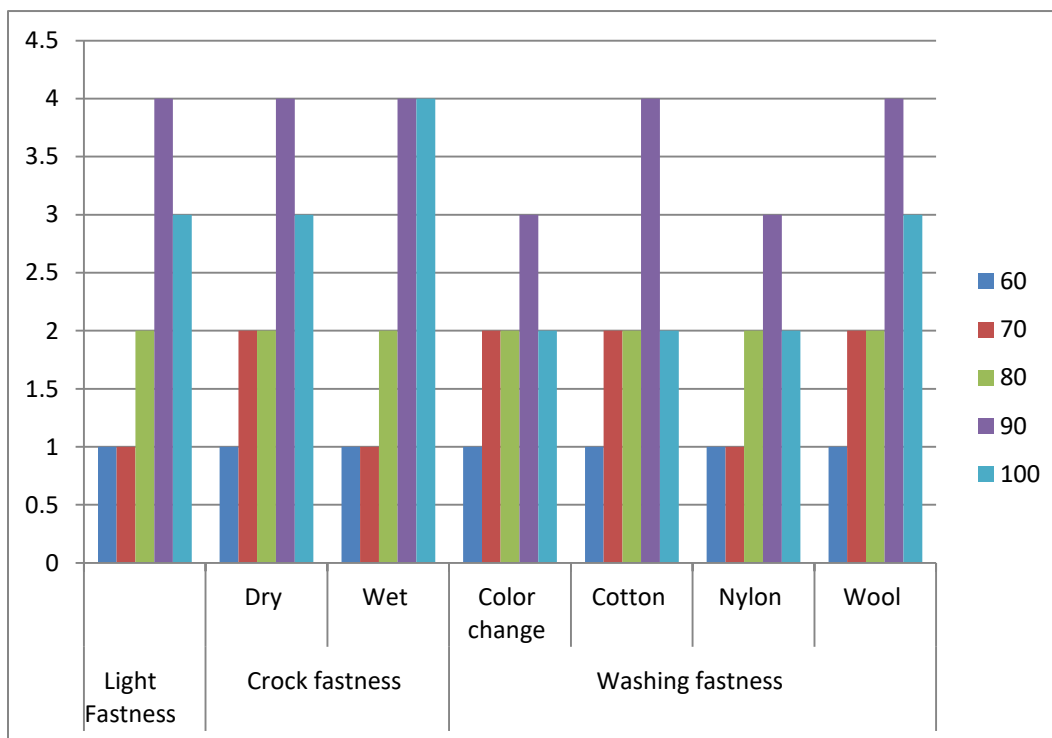


**Figure 4.5 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 2”**

**Dye-3**

Sr. No	Temperature °C	Light Fastness	Crock fastness		Washing fastness			
			Dry	Wet	Color change	Cotton	Nylon	Wool
1	60	2	1	1	2	1	2	2
2	70	2	1	2	2	2	2	2
3	80	3	2	2	2	3	2	2
4	90	4	3	3	3	4	3	3
5	100	3	3	3	2	2	3	3

**Table 4.15 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 3”**



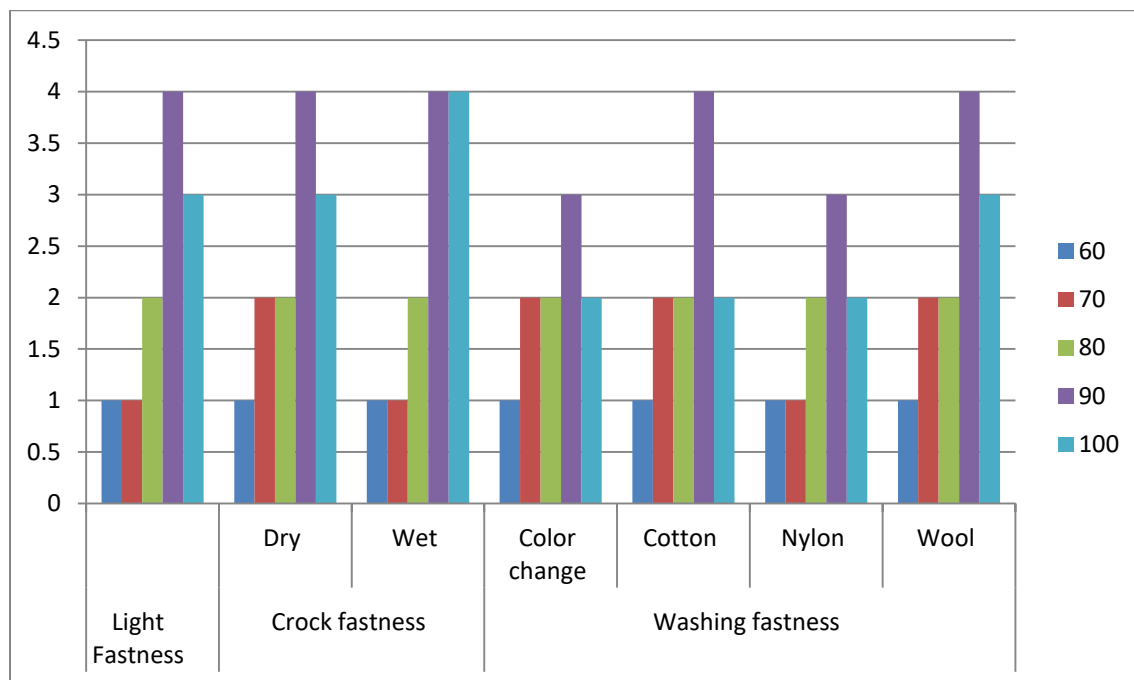
**Figure 4.6 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 3”**



**Dye-4**

Sr No	Temperature °C	Light Fast ness	Crock fastness		Washing fastness			
			Dry	Wet	Color change	Cotton	Nylon	Woo l
1	<b>60</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>	<b>1</b>
2	<b>70</b>	<b>2</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>1</b>	<b>2</b>
3	<b>80</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>1</b>	<b>2</b>
4	<b>90</b>	<b>3</b>	<b>4</b>	<b>3</b>	<b>3</b>	<b>2</b>	<b>3</b>	<b>3</b>
5	<b>100</b>	<b>3</b>	<b>3</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>2</b>	<b>3</b>

**Table 4.16 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 4”**



**Figure 4.7 “ Light Fastness-Crock Fastness-Washing Fastness Results of Dye 4”**

Dye-5

S r . N o	Temp eratur e °C	Lig ht Fas tne ss	Crock fastnes s		Washing fastness			
			Dr y	We t	Color change	Cotto n	Nylon	Wo ol
1	60	2	1	1	2	1	1	2
2	70	2	1	1	1	2	2	2
3	80	3	2	2	2	3	2	2
4	90	4	3	3	3	4	2	3
5	100	3	3	3	2	2	3	3

Table 4.17 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 5”

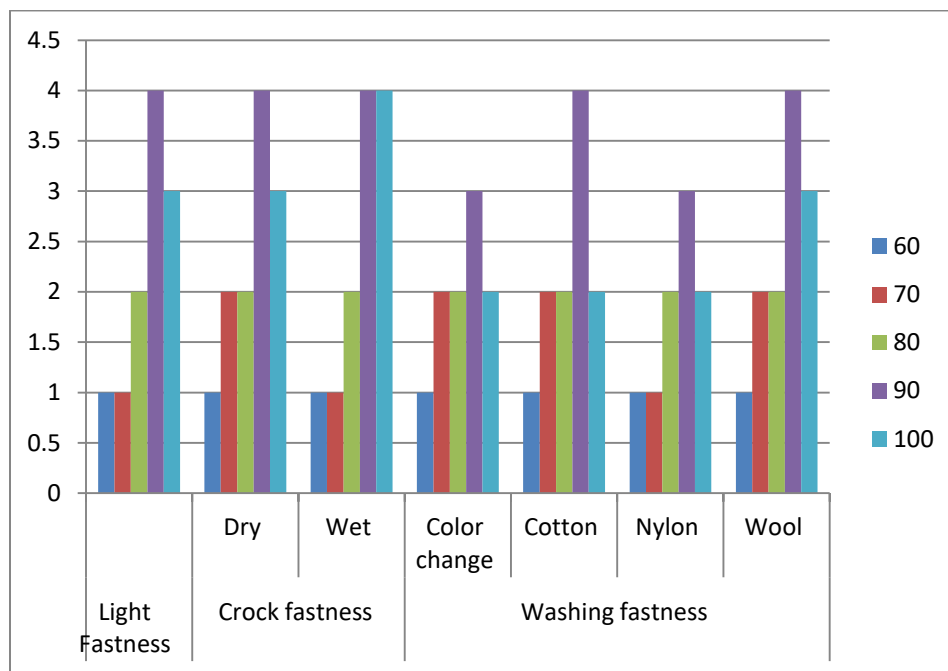
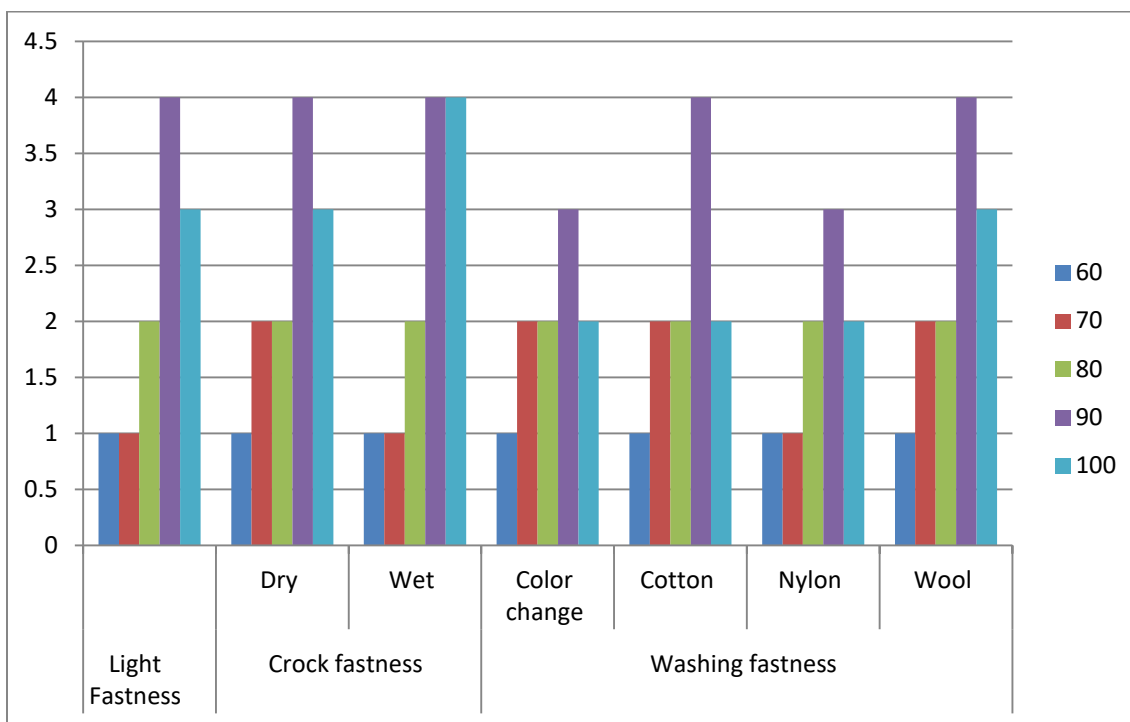


Figure 4.8 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 5”

**Dye-6**

Sr No	Temperature °C	Light Fast ness	Crock fastness		Washing fastness			
			Dry	Wet	Color change	Cotton	Nylon	Woo l
1	<b>60</b>	2	1	1	2	1	1	2
2	<b>70</b>	2	2	1	2	2	2	2
3	<b>80</b>	3	2	2	2	3	2	2
4	<b>90</b>	3	3	4	2	3	3	3
5	<b>100</b>	3	3	3	2	2	3	3

**Table 4.18 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 6”**

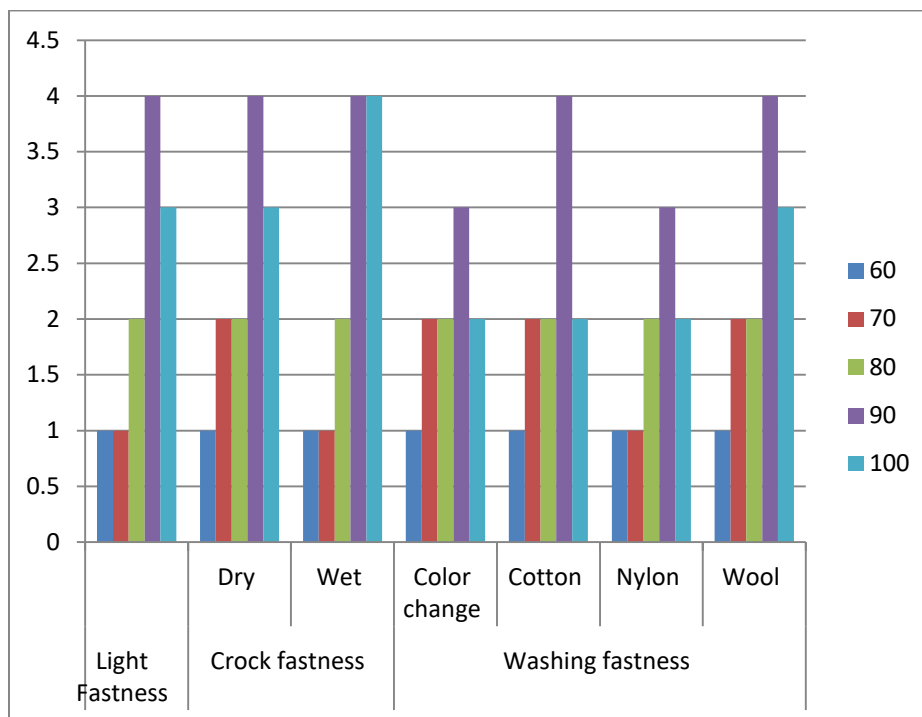


**Figure 4.9 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 6”**

**Dye-7**

S r . N o	Temp eratu re °C	Lig ht Fas tne ss	Crock fastne ss		Washing fastness			
			Dr y	We t	Color change	Cotto n	Nylon	Wo ol
1	60	1	2	1	1	3	1	1
2	70	1	2	1	2	4	2	1
3	80	2	2	2	2	4	2	2
4	90	3	4	4	3	4	3	4
5	100	3	3	4	3	2	2	3

**Table 4.19 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 7”**

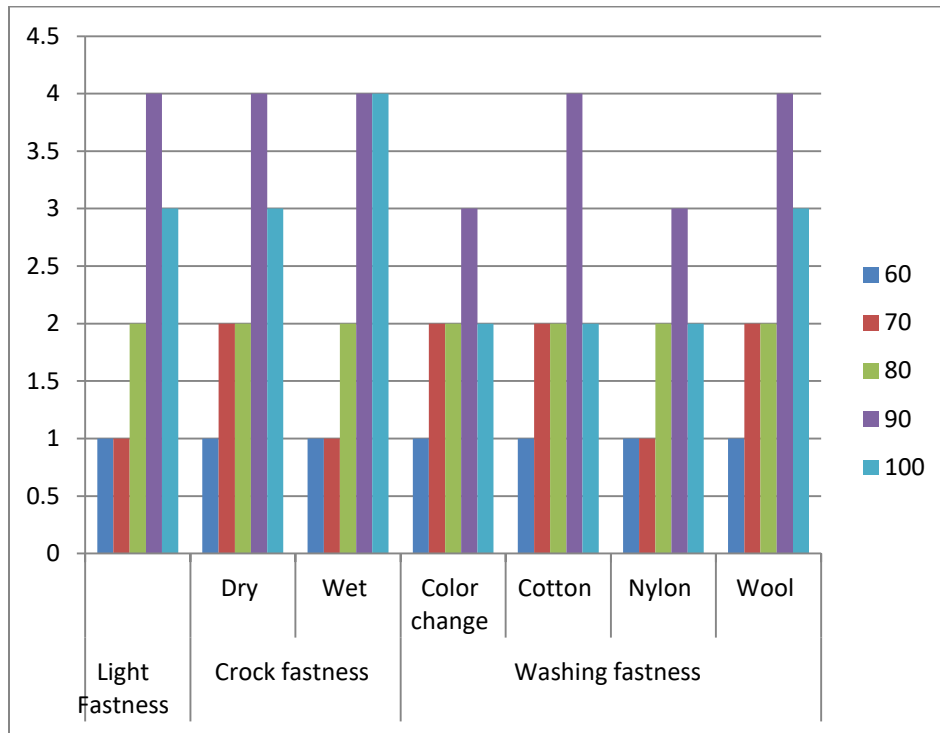


**Figure 4.10 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 7”**

**Dye-8**

S r . N o	Temp eratur e °C	Lig ht Fas tne ss	Crock fastnes s		Washing fastness			
			Dr y	We t	Color change	Cotto n	Nylon	Wo ol
1	60	1	1	1	1	1	1	1
2	70	1	2	1	2	2	1	2
3	80	2	2	2	2	2	2	2
4	90	4	4	4	3	4	3	4
5	100	3	3	4	2	2	2	3

**Table 4.20 “Light Fastness-Crock Fastness-Washing Fastness Results of Dye 8”**



**Figure 4.11 “ Light Fastness-Crock Fastness-Washing Fastness Results of Dye 8”**

#### 4.4.5 Color strength K/S by Kubelka-Munk equation

$$\text{“K/S} = ((1.0 - R_\lambda)^2 / (2.0 R_\lambda)\text{”}$$

Where  $R_\lambda$  is the reflectance of fabric at  $\lambda_{\max}$

Dye no.	Wavelength $\lambda_{\max}$	Absorbance	K/s
1	575	0.13	2.91
2	520.9	0.12	3.23
3	534.9	0.14	2.64
4	540.3	0.17	2.03
5	480	0.08	5.29
6	510.8	0.18	1.87
7	533.6	0.16	2.21
8	475.7	1.2	0.02

Table 4.21 Kubelka-Munk equation formulation

#### 4.5 Fourier Transform Infrared Spectroscopy Technique (FTIR)



Figure 4.12 A FTIR Device

Fourier-transform-infrared-spectroscopy (FTIR) is a characterization technique. It can be used to study;

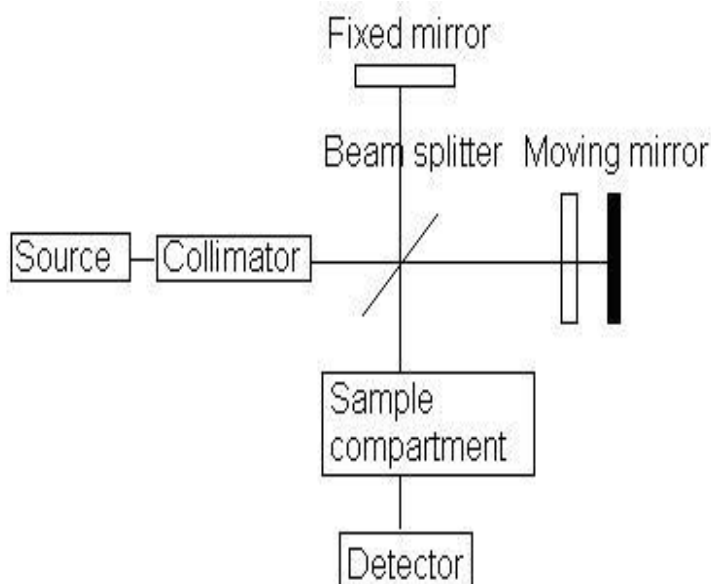
- photoconductivity
- Raman scattering,
- infrared spectrum of absorption and emission

By FTIR spectrometer, high spectral-resolution-data for an ample range of spectrum is obtained. Fourier transformation is applied by this technique to modify data in a real spectrum.

The basic aim of FTIR is to determine the light-absorbance of a sample, over a range of wavelength. So a beam of monochromatic light is applied on the sample to measure its absorbance. This procedure is repeated for all the wavelengths and the computer processes the acquired data to get absorption at each wavelength by Fourier transformation.

It also provides spectral information regarding

- Sample's atomic bonding
- Carbon and Oxygen related functional groups



**Figure 4.13 Schematic Diagram of FTIR**

Infrared spectroscopy is a technique uses the electromagnetic radiations to determine functional groups which are present in a molecule.

The bonds present in a molecules are continuously vibrate with some frequency ( $f$ ) and wavelength ( $\lambda$ ) combine with relation

$$c = \lambda \nu$$

Where  $c = 3.0 \times 10^8$  m/s

Since molecular vibrations follow hook's law

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m_1 + m_2}} \quad \dots\dots\dots(2)$$

where  $k$  = spring stiffness coefficient of bond

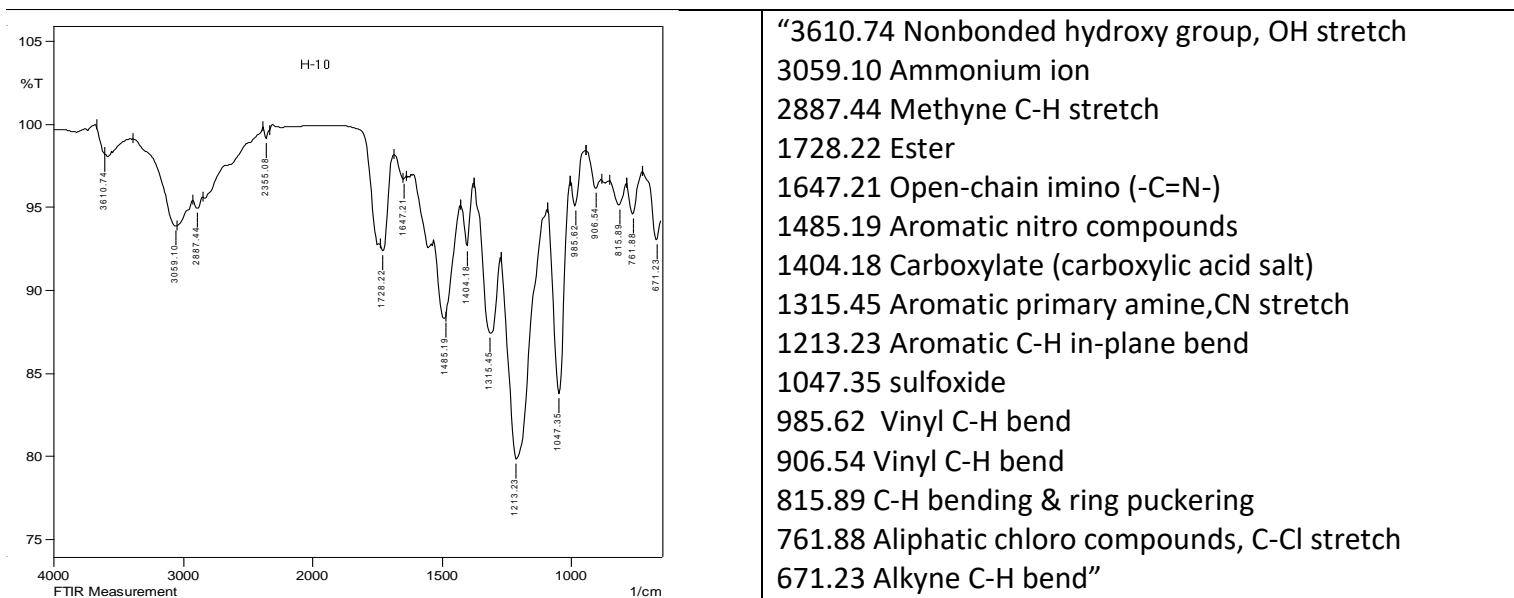
$f$  = force constant

$n = 2$  tells that molecular vibrations depend on following two factors

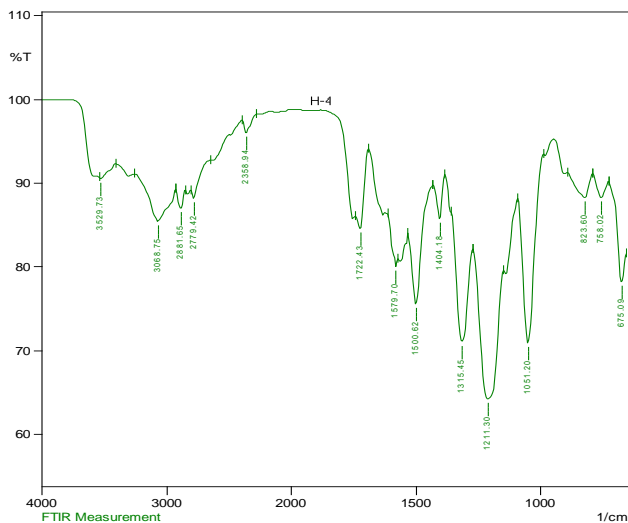
1-Mass of atoms involved

2-Strength of bond between them

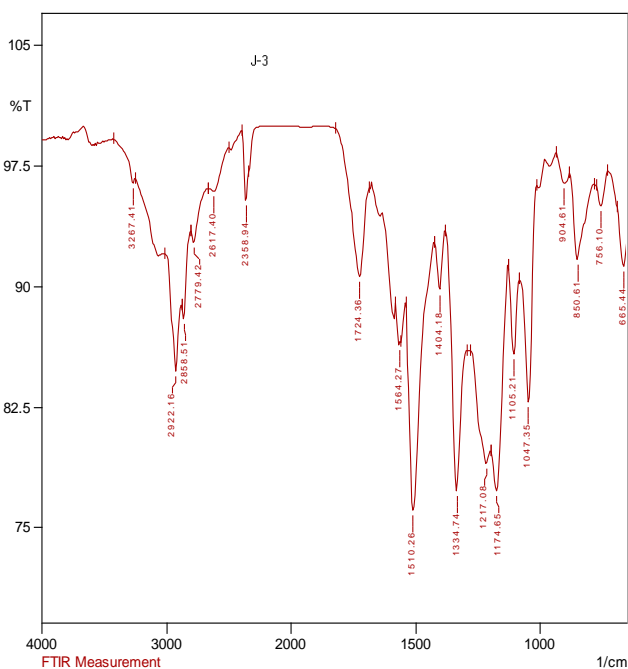
Hence molecules with strong bonds oscillate with higher frequencies , wave number  $1/\lambda$  and low wavelength ( $\lambda$ ).



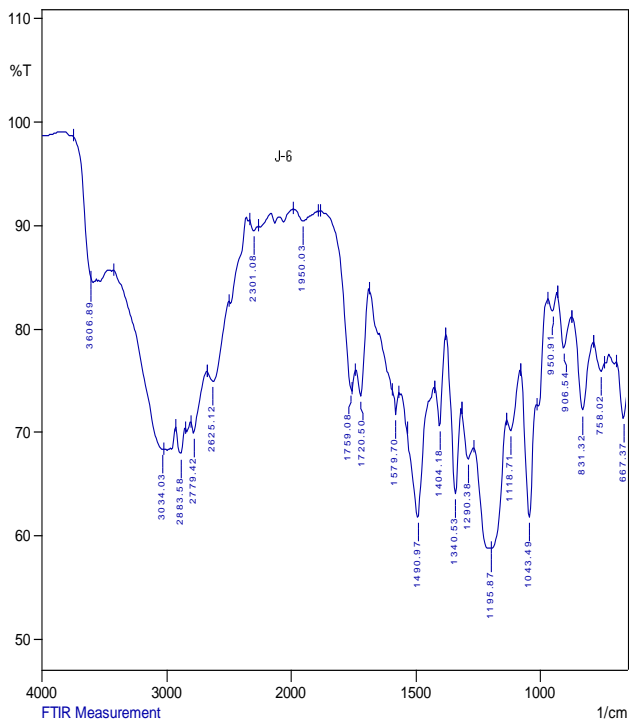




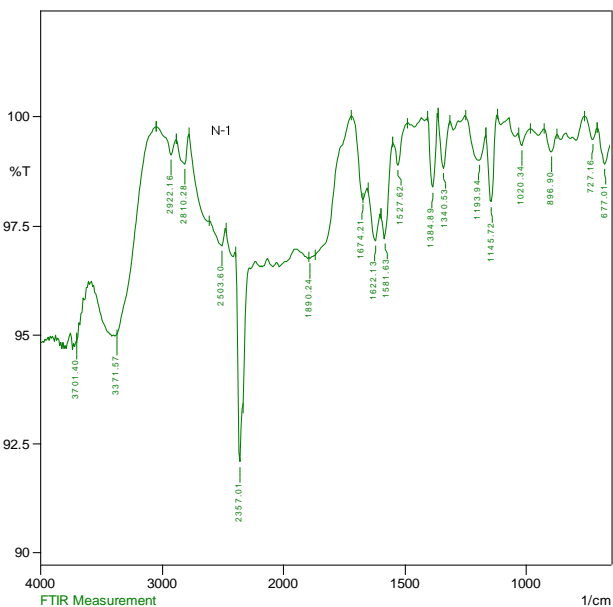
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 3068.75 Ammonium ion  
 2881.65 Methyne C-H stretch  
 2779.42 C-H (aldehyde C-H)  
 1722.43 Ester  
 1579.7 Open-chain azo (-N=N-)  
 1500.62 Aromatic nitro compounds  
 1404.18 Carboxylate (carboxylic acid salt)  
 1315.45 Aromatic primary amine, CN stretch  
 1211.30 Aromatic C-H in-plane bend  
 1051.2 C-O stretch  
 823.60 Peroxides, C-O-O-stretch  
 758.02 C-H bending & ring puckering  
 675.09 Alcohol, OH out-of-plane bend"



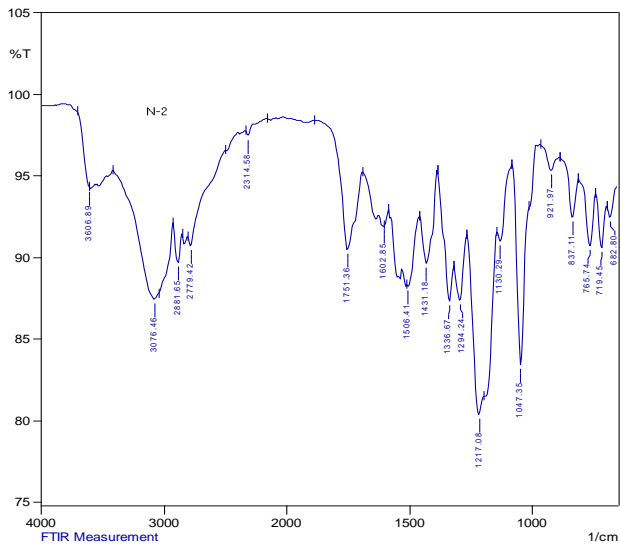
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 2922.16 Methyl C-H asym./sym. stretch  
 2779.42 C-H (aldehyde C-H)  
 1724.36 Ester  
 1564.27 Aliphatic nitro compounds  
 1510.26 Aromatic nitro compounds  
 1404.18 Carboxylate (carboxylic acid salt)  
 1334.74 Aromatic secondary amine, CN stretch  
 1217.08 Aromatic C-H in-plane bend  
 1174.65 Secondary amine,  
 1105.21 C-O stretch  
 1047.35 Cyclohexane ring vibrations  
 904.61 Vinyl C-H bend  
 850.61 Peroxides, C-O-O-stretch  
 756.10 C-H bending & ring puckering  
 665.4 Alcohol, OH out-of-plane bend"



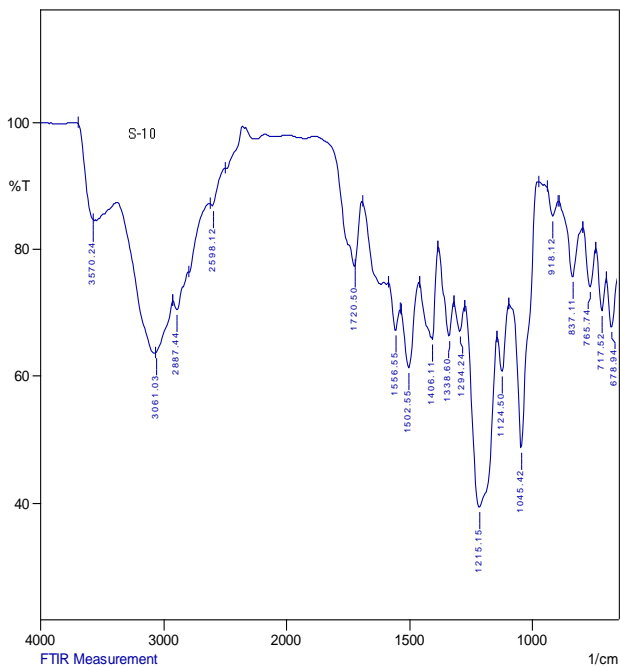
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 2883.58 Methyne C-H stretch  
 2779.42 Aldehyde  
 2625.12 C≡C stretch  
 1950.03 C=C asymmetric stretch  
 1720.50 Ester  
 1579.7 Open-chain azo (-N=N-)  
 1490.97 Aromatic nitro compounds  
 1404.18 Carboxylate (carboxylic acid salt)  
 1340.53 Aromatic tertiary amine, CN stretch  
 1290.38 amino, C-N  
 1195.87 Tertiary amine, CN  
 1118.71 C-O stretch  
 1043.49 Cyclohexane ring vibrations  
 950 *trans*-C-H out-of-plane bend  
 831 Peroxide, C-OO  
 758 C-H bending & ring puckering  
 667 OH stretch”



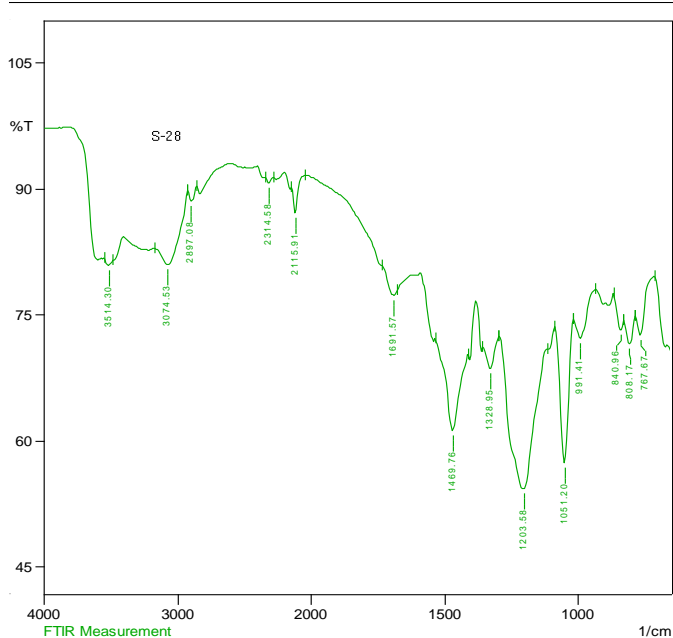
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 3371 NH -stretch  
 2922 C-H -asym-stretch  
 2810 Methoxy,- C-H stretch (CH<sub>3</sub>-O-)  
 1674 Open-chain- imino (-C=N-)  
 1622 Open-chain -azo (-N=N-)  
 1581 Open-chain- azo (-N=N-)  
 1527 Aromatic --nitro compounds  
 1384 Carboxylate- (carboxylic acid salt)  
 1340 sulfonic- acid  
 1193 Tertiary amine,- CN stretch  
 1145 C-O -stretch  
 1020 Cyclohexane ring vibrations  
 896 Vinyl C-H -bend”



“3606 Phenols, OH stretch  
 3076 Aromatic C-H stretch  
 2779 Aldehyde  
 1751 C=O  
 1602 Open-chain azo (-N=N-)  
 1506 Aromatic nitro compounds  
 1217 Aromatic C-H in-plane bend  
 1047 Cyclohexane ring vibrations  
 765 C-H bending & ring puckering  
 719 Methylene  $-(CH_2)_n-$ ”



“3570 OH stretch  
 3061 Ammonium ion  
 2887 Methyne C-H stretch  
 2598 C≡C stretch  
 1720 Ester  
 1556 N-H (2i-amide) II band  
 1502 Aromatic nitro compounds  
 1406 Carboxylate (carboxylic acid salt)  
 1338 Aromatic tertiary amine, CN stretch  
 1294 Aromatic secondary amine, CN stretch  
 1215 Aromatic C-H in-plane bend  
 1124 C-O stretch  
 1045 Cyclohexane ring vibrations  
 918 Vinyl C-H bend  
 837 Peroxides, C-O-O-stretch  
 765 C-H bending & ring puckering  
 717 Methylene  $-(CH_2)_n-$   
 678 Alcohol, OH out-of-plane bend”



“3514 OH stretch  
 3074 Aromatic C-H stretch  
 2897 Carboxylic Acid O-H Stretch  
 2115 -N=C=O  
 1691 Open-chain imino (-C=N-)  
 1469 1328 Aromatic tertiary amine, CN stretch  
 1203 Aromatic C-H in-plane bend  
 1051 C-O stretch  
 991 Vinyl C-H bend  
 840 Peroxides, C-O-O-stretch  
 808 Alcohol, OH out-of-plane bend  
 767 C-H bending & ring puckering”

**Figure 4.14 FTIR Results Interpretation**

## 4.6 Conclusions and Future work

Eight Bifunctional diazo Direct Dyes synthesized (table ) and characterized by Fourier transform infrared spectroscopy and Ultra violet spectrophotometer. Wave lengths  $\lambda$  ranges from 475-575 nm within visible spectrum. Best Fastness i.e 3~4 properties are observed at Temperature range of 80-90 ° C at fix Liquor ratio of 60:1,pH 7.0,Time 30 min and Salt concentration of 10% as shown in graphs.

Color Coordinates were also checked with color meter and results shows good Hue and chroma values.

Color Strength K/s checked by Kubelka Munk equation and best K/s value 5.29 observed against  $\lambda_{\max}$  480nm.

The results indicate good solubility high degree of exhaustion and fixation, good fastness and high substantivity over the knitted cotton fabrics.

### Future Recommendation

- Further coupling of Urea based direct dyes with poly azo chromogens.

- Mutagenicity testing
- Adsorptive behavior of urea based dyes
- Optimization of dyeing by varying physical parameters
- To investigate color strength  $K/s$  against different physical parameters

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