

# Study of synthesis, molecular structure and application characterization of a novel stilbene based diazo direct fibre dye for dyeing various fibres

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**Abstract:** Colors are shaded mixes which are used for passing on shading to the silk, nourishment stuffs, materials and fleece. Direct dyes were at first familiar fiscally for application with cellulosic fibers and this was so far their most essential use. The improvement rate of direct dyes for cellulosic strands was depended upon to continue growing. The present research work was related to prepare of new 4,4-diamino biphenyl stilbene - 2,2-disulphonic destructive based direct shading. This prompt shading was organized by methods for buildup, diazotization, hydrolysis and coupling forms. The joined shading had been associated on cellulosic material by debilitate process. Shaded surface qualities moreover had been concentrated, for instance, light speed, rubbing snappiness and washing speed. Application qualities like salt focus, pH, shading temperature and shading time were moreover shown. The fundamental depiction of consolidated 4,4-diamino biphenyl stilbene - 2,2-disulphonic destructive based direct shading were done with fourier change infrared spectroscopy (FT-IR).

## Chapter 1

### INTRODUCTION

#### 1.1 Concise history of dyes

In the first place, colors were gotten from normally happening sources (creatures, vegetables and minerals) e.g. tyrian purple, cochineal, madder, indigo, Prussian blue and ultramarine. The craft of coloring was known in China since 3000 BC. Fiber responsive colors comprise of a particle having labile gathering. It can frame stable covalent bonds with cellulose [1]. The quick utilization of fiber responsive colors has two fundamental explanations behind cellulosic material. To begin with, it has stable application on texture with minimal effort. Also, these colors have attractive speed to wet treatment because of covalent holding amongst texture and color particles [2].

A color is a characteristic intensify that can take up some wavelength of the shaft dropping on it. The staying of the bar is reflected. The reflected light will at last contain shading adjusting to that of the ingested. A color may dismantle up every observable bar from one wavelength which might be reflected. The color will contain shade of the reflected wavelength [3].

Coordinate color is a class of dyestuffs that are associated direct to the substrate in a fair or acid neutralizer shower. They convey full shades on cotton and material without directing and can in like manner be associated with rayon, silk, and wool. Organize hues give wonderful shades yet show poor wash speed. Distinctive after solutions are used to improve the wash snappiness of direct hues and such hues are suggested as after treated direct tints. Facilitate hues are used on cotton, paper, calfskin, wool, silk and nylon. They are also used as pH markers and as natural stains. Shading is the route toward adding shading to material things like strands, yarns, and surfaces. Shading is regularly done in a novel game plan containing hues and manufactured material. Resulting to shading, shading iotas have uncut Chemical bond with fiber particles. The temperature and time controlling are two key thinks about shading. There are generally two classes of shading, trademark and artificial [4].

Shading of materials has been practiced for a substantial number of years with the fundamental made record out of the usage of dyestuff dated at 2600 BC in China. All hues

were basic substances gotten from plant, animal or mineral sources. In 1856, William Henry Perkin, while chasing down a cure for wilderness fever, found the fundamental produced shading, Mauve. The mauve shading was mind blowing fuchsia shading, yet obscured viably. Since that time, a mind boggling number of built hues have been made and their impenetrability to running and obscuring has been almost wiped out. All bits of attire got today are hues with made hues. Organize colors are colorants that can shading cellulosic strands without the prerequisite for a pre-treatment of the fibers with stringent [5]. The principle coordinate shading for cotton was Congo red which was found by Professor Paul Boettiger in 1884 [6]. The quick molecule can interface by methods for hydrogen holding and van der waal powers. Shockingly, this kind of holding between coordinate hues and cellulose isn't satisfactory to yield extraordinary wash snappiness. Organize hues are calm to create. Besides, they give a fundamental and for the most part sensible strategy for shading cellulosic strands. Despite their use on cotton and rayon, organize hues are fundamental in shading of calfskin and the tone of paper [7].

Arrange hues are open in all shades and in generous numbers. Nevertheless, the greater part of these hues give dull shades. Benzedrine's constituted-based direct hues are a basic class of direct hues. Regardless, they speak to an immense risk to human prosperity and

didn't generally convey in numerous countries. Inspect in potential substitution for Benzadrine has carried on by analysts in different labs.

Benzadrine and other confined amines have made a deficiency in shading industry, since countless were being prepared from them. The interior organization for look into on tumor has surveyed the growth causing nature of a huge part of the colorants in light of limited amines including Benzadrine and its subordinates. Since limited amines based colorants and intermediates have unending perils of growth causing nature and all negatively powerless sensation, from now on it has incited filter for eco-obliging non-genotoxic decisions for hues.

The murdering sway is by all record by all account not the only reason behind the limit of the extra salt to drive the quick shading into the fiber. The colleague of a strong electrolyte with a shading shower would altogether be able to diminish arrange hues the dissolvability of the hues in the shower and cause the mixture of colors [8]. Before long, day shower weariness is controlled by the extension of electrolyte and the bearing of the shading shower temperature.

The development of electrolyte to the shading shower murders the surface charge, empowering the shading anions to approach the fiber, Suitable electrolyte to the shading shower executes the surface charge, enabling the shading anions to approach the fiber .Suitable electrolyte is ordinary salt sodium chloride or sodium sulfite [9].

Color is a natural or engineered shading material that is used in answer for discolor materials especially cellulosic fiber. Each shaded material isn't colors. A shaded issue is known as a color in the event that it finishes the consequent states. It must contain proper shading. It can be joined on the cellulosic fiber either in a straight line or with the help of entering. At the point when color is joined to cellulosic fiber, it must rush to light and washing. It must be against activity of alkalies, water and acids.

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## Chapter-2

## MATERIALS AND METHODS

The blend and compound portrayal of orchestrated 4,4-diamino biphenyl stilbene - 2,2-disulphonic corrosive based direct color had been talked about here. The amalgamation of color was finished in Harris colors and shades industry in Faisalabad. The distinctive synthetic portrayal and examination were finished in a joint effort with Pakistan Council Scientific and Industrial Research (PCSIR) labs complex Lahore.

### 2.1 Equipments

Every single business reagent and solvents associated with the combination were of logical review and were used as gotten. Strong crude materials utilized for the amalgamation of colors were taken from Harris colors and chemicals private restricted Faisalabad.

### 2.2 Devices utilized in experimental work

Electric stirrer, water bath, pH meter, glass beaker 1L and 2L, thermometer 10°C-110°C, funnel, flask, pipette, measuring cylinder and drying oven.

Digital pH meter (Hanna 9818).

U-2001 Shimadzu (Japan) fourier transform infrared spectrometer (FT-IR) was used at Pakistan council for scientific and industrial research (PCSIR) Lahore.

Lab scale exhaust dyeing machine was used for the dyeing process.

### 2.3 Utilized chemicals as analytical grade

Na<sub>2</sub>CO<sub>3</sub>, HCl, sodium nitrite, cynuric chloride, 4,4-diamino biphenyl stilbene -2,2-disulphonic acid, 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid and 2,4,6-trichloro-1,3,5-triazine

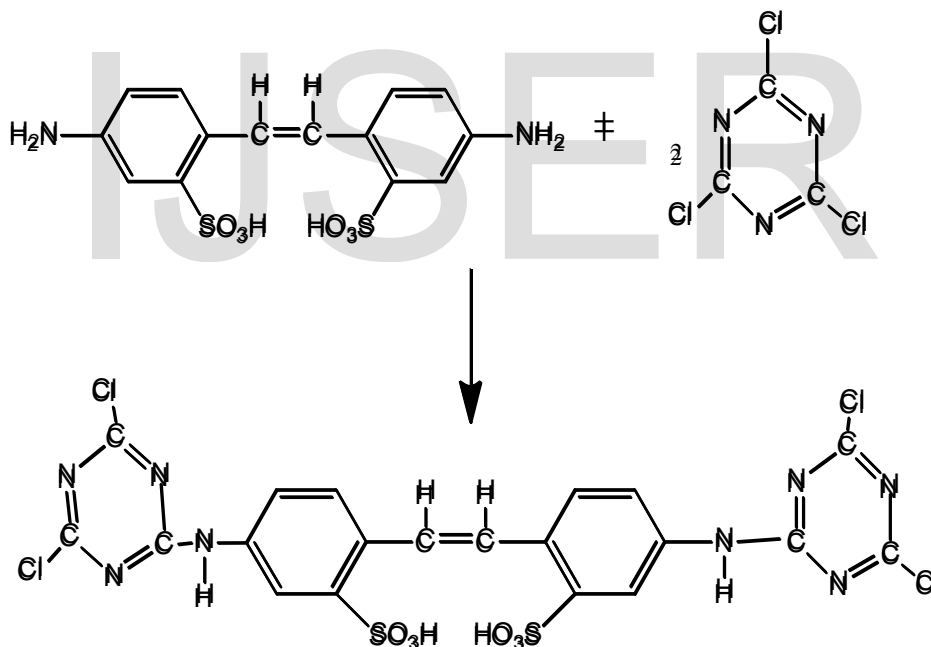
### 2.4 Scheme to synthesize direct dye

Direct dye is prepared by 4,4-diamino biphenyl stilbene -2,2-disulphonic acid. The dye is prepared in 1000 mL beaker containing 50 mL water. This direct dye has been synthesized by coupling and condensation components. Dying and exhaust method are used [10]. Industrial characterization is studied like fastness per industrial standards society of dyers and colourist.

### 2.5 Synthesis route for the direct dye

### 2.5.1 Condensation

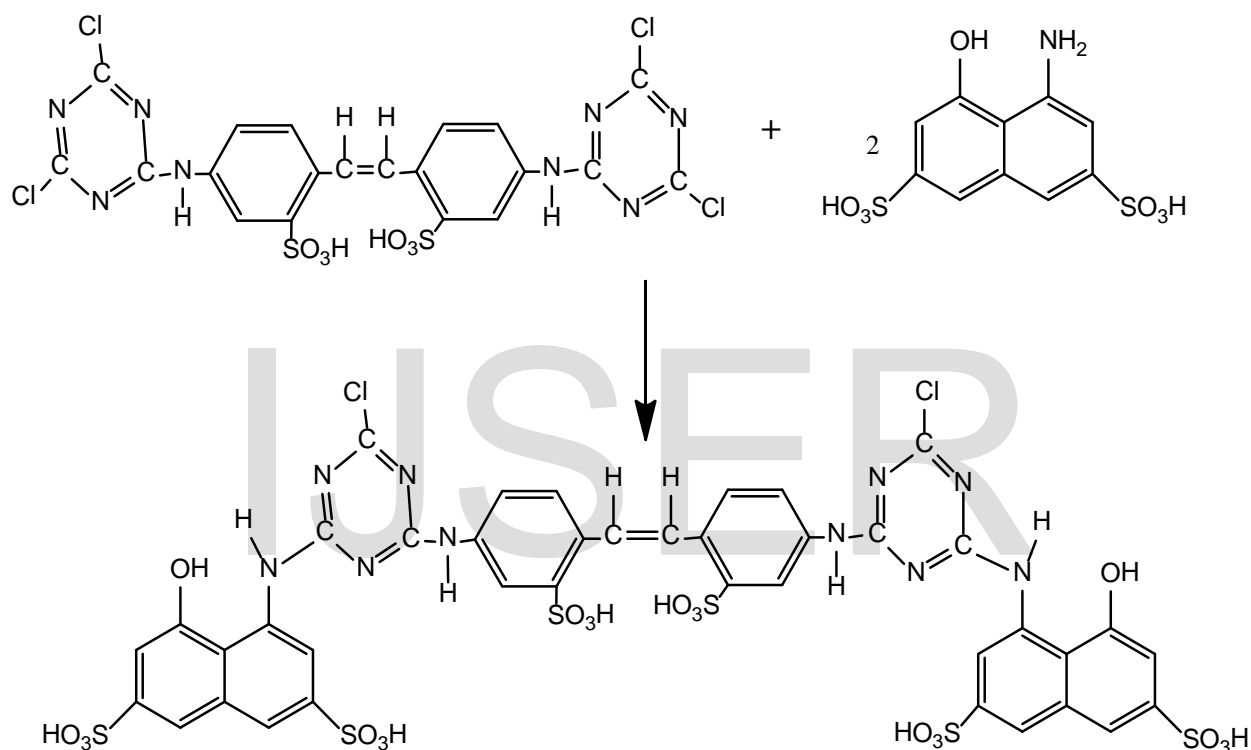
In the suspension of 0.04 mole of 2,4,6-trichloro-1,3,5-triazine (cyanuric corrosive 4g/25mL), 50 mL arrangement 0.02 mole of 4,4-diamino biphenyl stilbene - 2,2-disulphonic corrosive (80%) was poured drop astute. The response blend was consolidated at consistent mixing for 1.5 hours at response states of pH 1.5-2 and temperature 0°C-5°C. To start with buildup was inspected chromatographically on Whattman channel paper No. 1 by utilizing 2% sodium chloride arrangement as eluent. At that point, N,N-dimethyl benzaldehyde was splashed. The consolidated item was sifted. 100 mL of 1-amino-8-hydroxynaphthalene-3,6-disulphonic corrosive (0.04 moles and pH 7) was added to consolidated item without a moment's delay. This blend was warmed gradually up to 45°C and was mixed for an hour for the consummation of second buildup at pH 6-6.5. The pH was kept up by 20% Na<sub>2</sub>CO<sub>3</sub> arrangement. It is appeared in figure 2.1.



**Figure 2.1** Condensation of 2,4,6-trichloro-1,3,5-triazine (cyanuric acid) with 4,4-diamino biphenyl stilbene -2,2-disulphonic acid

### 2.5.2 Condensation of above product obtained in figure 3.1 with H-acid

100 mL of 1-amino-8-hydroxynaphthalene-3,6-disulphonic corrosive (0.04 moles and pH 7) was added to consolidated item acquired in article 3.6.2 without a moment's delay. This blend was warmed gradually up to 45°C and was mixed for a hour for the fruition of second buildup at pH 6-6.5. The pH was kept up by 20% Na<sub>2</sub>CO<sub>3</sub> arrangement. The response blend was again warmed up to 95°C-100°C with changing pH at 11-12 and mixed for 60 minutes. The subsequent dense item was again analyzed chromatographically modifying pH 7 by including little measure of hydrochloric corrosive (33% unadulterated HCl). This response is spoken to in figure 2.2.



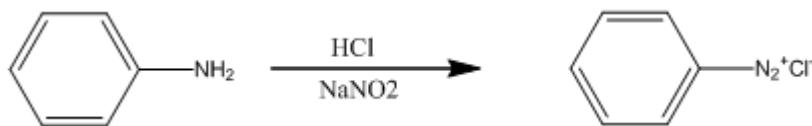
**Figure 2.2** Condensation of product obtained in figure 2.1 with 1-amino-8-hydroxy naphthalene-3,6-disulphonic acid (H-acid).

### 2.5.3 Diazotization of aniline

Diazotization was done by dissolving 200 mL H<sub>2</sub>O and aniline (95% unadulterated and 0.04 moles) into 150 mL of hydrochloric corrosive (33% unadulterated). The response blend was additionally mixed for an hour at 0°C. 50 mL of 0.04 mole of sodium nitrite arrangement was emptied drop astute into aniline response blend and mixed for 1.5 hours. The diazotized item arrangement was checked with iodine starch marker paper little amount of sulfamic corrosive



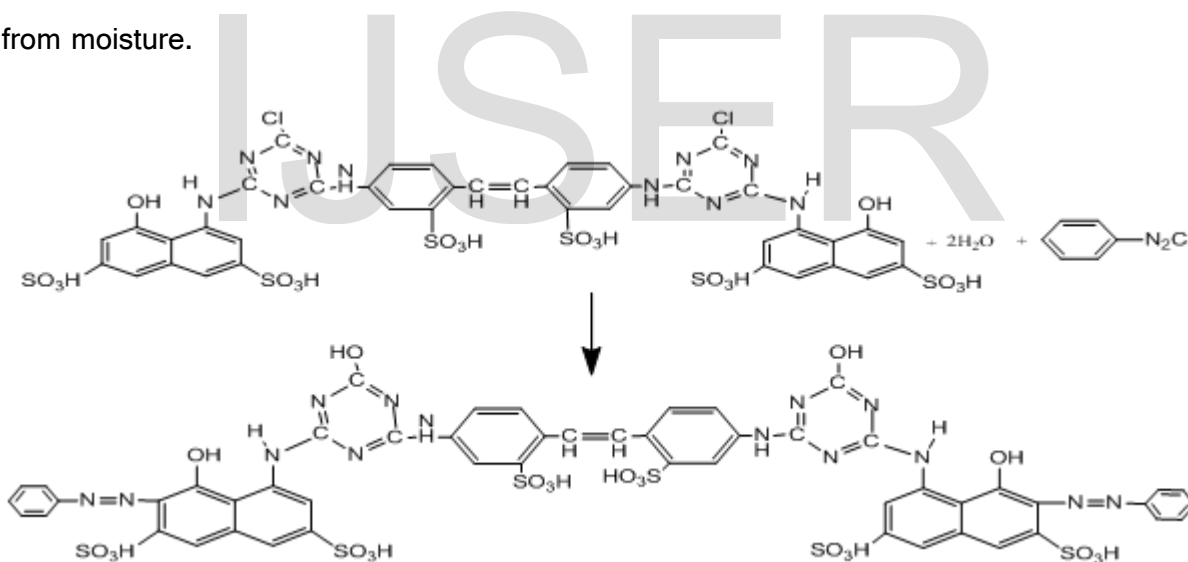
( $\text{H}_3^+\text{NSO}_3^-$ ) was additionally added to the diazotized item. Diazotization is appeared in figure 2.3.



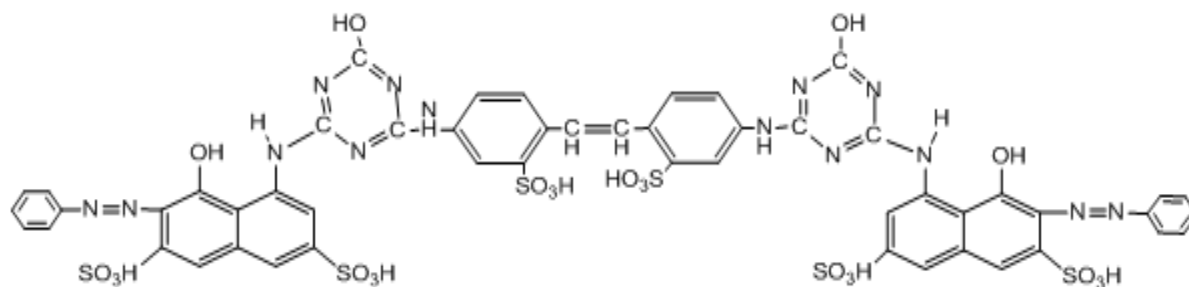
**Figure 2.3** Diazotization of aniline by adding hydrochloric acid and sodium nitrite.

### 2.5.4 Hydrolysis and coupling process

Hydrolysis had been carried out. Then 0.04 moles of diazotized aniline was coupled with the above condensate. After coupling, dye solution was dried in oven at 80 °C -90 °C. After drying dye was grinding in pester and mortar. Then grinding dye was stored in bottle to save it from moisture.



**Figure 2.4** Hydrolysis and coupling process of diazotized aniline with condensed product obtained in figure 2.2.



**Figure 2.5** Chemical structure of prepared direct dye obtained through condensation, diazotization and coupling process.

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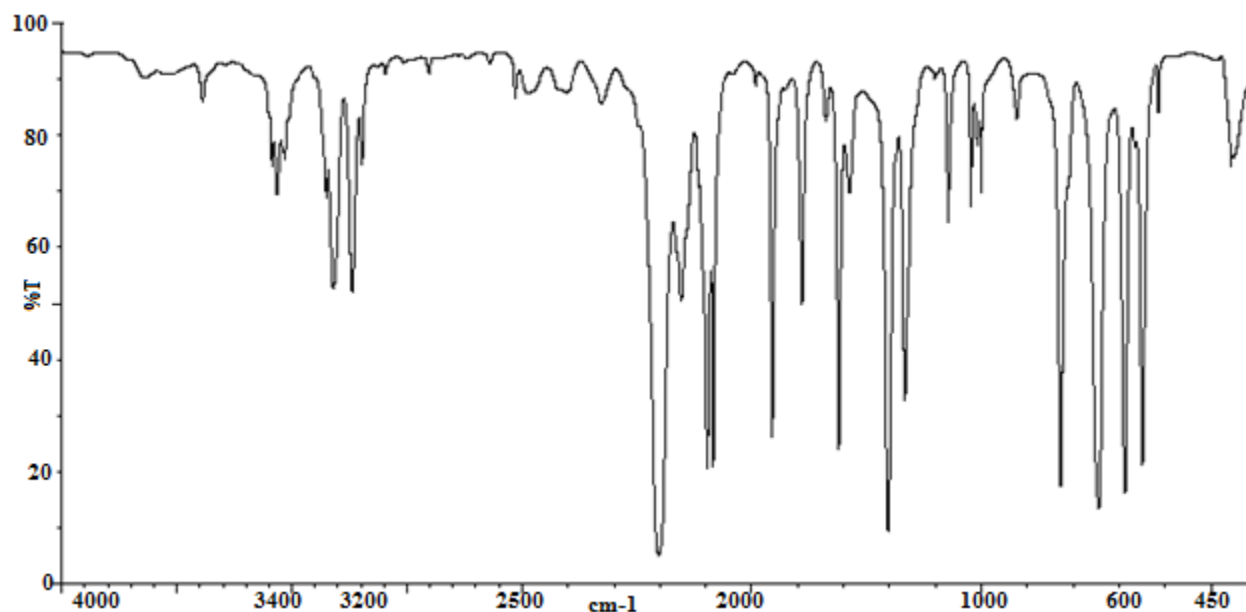
## **Chapter-3**

### **Results and discussion**

#### **3.1 Determination of functional groups by fourier transforms infra red spectrophotometer (FT-IR)**

Fourier change infrared spectroscopy (FT-IR) is an exceptionally useful procedure which is utilized to distinguish piece, chain introduction and quantitative estimations in an obscure blend. A FT-IR spectrometer is an instrument that acquires broadband range. It is a strategy of

accomplishing infrared spectra. It initially gathers an interferogram of an example flag utilizing an interferometer. At that point it plays out a fourier change on interferogram to accomplish the range. Amid the association of radiation with the example, some infrared radiations are consumed by the specimen. A few radiations went through the specimen. The subsequent range demonstrates the sub-atomic transmission and ingestion. Along these lines, it makes a sub-atomic unique mark of the example. FT-IR has infrared district in the range 4000-400  $\text{cm}^{-1}$ . Two sub-atomic structures can't have a similar infrared range like unique mark area. This technique can recognize obscure compound and examine the basic highlights like practical gatherings. This system can likewise be utilized to decide the amount of parts display in the specimen. Trademark bunches for coordinate shading at broadening repeat are discussed here. Absorbance peak of  $\text{-C=C-}$  appeared at  $3096 \text{ cm}^{-1}$ . The  $\text{N=N}$  frequency in plane appeared in the range of  $1490.99 \text{ cm}^{-1}$ . Whereas, the peaks recorded at  $1150 \text{ cm}^{-1}$  were assigned for  $\text{-OSO}_3\text{H}$  stretching. Absorbance peak of  $\text{-C-N}$  appeared at  $1147.35 \text{ cm}^{-1}$ . The  $\text{-SO}_2$  stretching band is in the region of  $1108 \text{ cm}^{-1}$ . The  $\text{-NH}$  and  $\text{-OH}$  frequency in plane appeared in the range of  $3410 \text{ cm}^{-1}$  and  $3629.90 \text{ cm}^{-1}$ . Various substituted benzene rings show absorbance band in the region of  $1007 \text{ cm}^{-1}$  and  $845 \text{ cm}^{-1}$ .



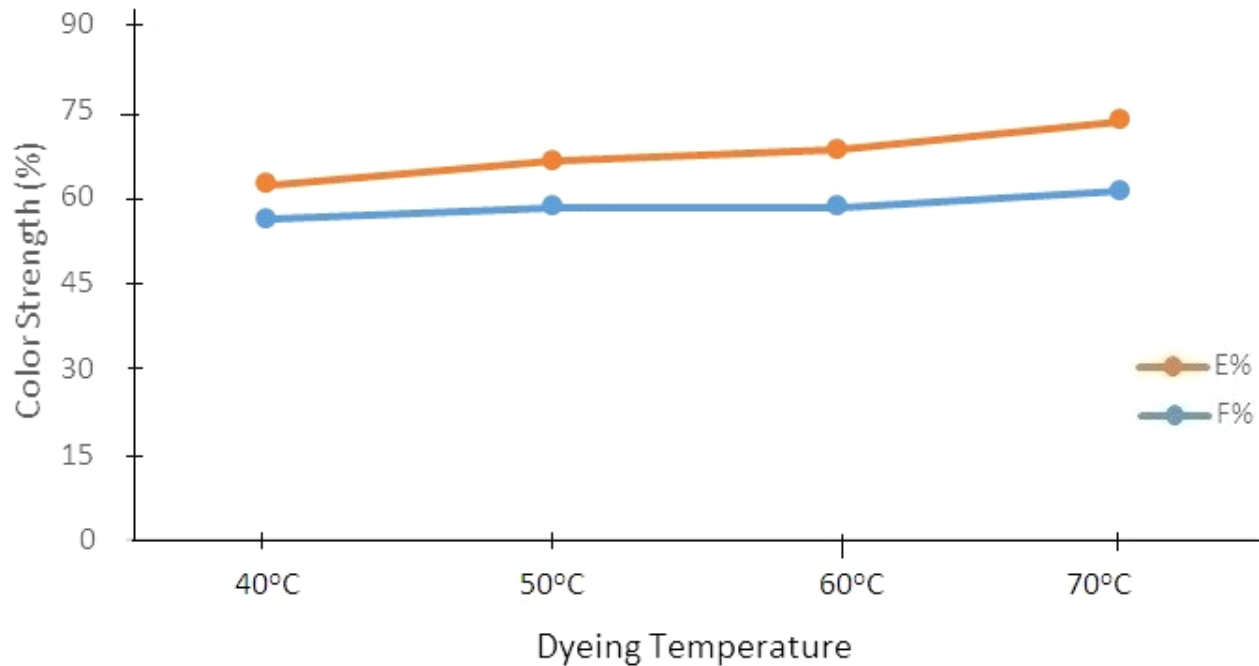
**Figure 3.1** FT-IR spectrum of synthesized direct dye

**Table 3.1** Stretching and bending frequencies of characteristics functional groups present in prepared direct dye.

Characteristics Peak (cm <sup>-1</sup> )	Assignment	Functional Group
3410	-NH Stretching	-NH-
1490.99	-N=N- stretching	-N=N-
1108	S=O Stretching	-SO <sub>2</sub>
3096	-C=C Stretching	-C=C-
1560.33	-C=C Stretching	Aromatic rings
1007, 845	Substituted benzene rings	Benzene rings
1150	-OSO <sub>3</sub> H stretching	-OSO <sub>3</sub> H
3629.90	-O-H Stretching	-O-H
1147.35	-C-N stretching	-C-N

### 3.2 Effect of shading temperature on (%) shading quality

Temperature is to an awesome degree real part to shading process since shading at low temperature most likely stays insufficient and high temperature may prompts the debasement and desorption of the tones. To impel the impact of direct temperature on the cushion pack shading, cotton surface was toned at various temperatures i.e. 40 °C, 50 °C, 60 °C and 70 °C. The information picked up has been plotted in the figure 3.2 for the planned tints. Most critical shading quality was seen at 70 °C for the orchestrated direct shading. Temperature more than 70 °C chops down the shading quality respect which may be an immediate aftereffect of desorption of the shading particles from the surface to the shading shower by moving its change. The shading quality got for arranged direct color at 70 °C was 76 %.

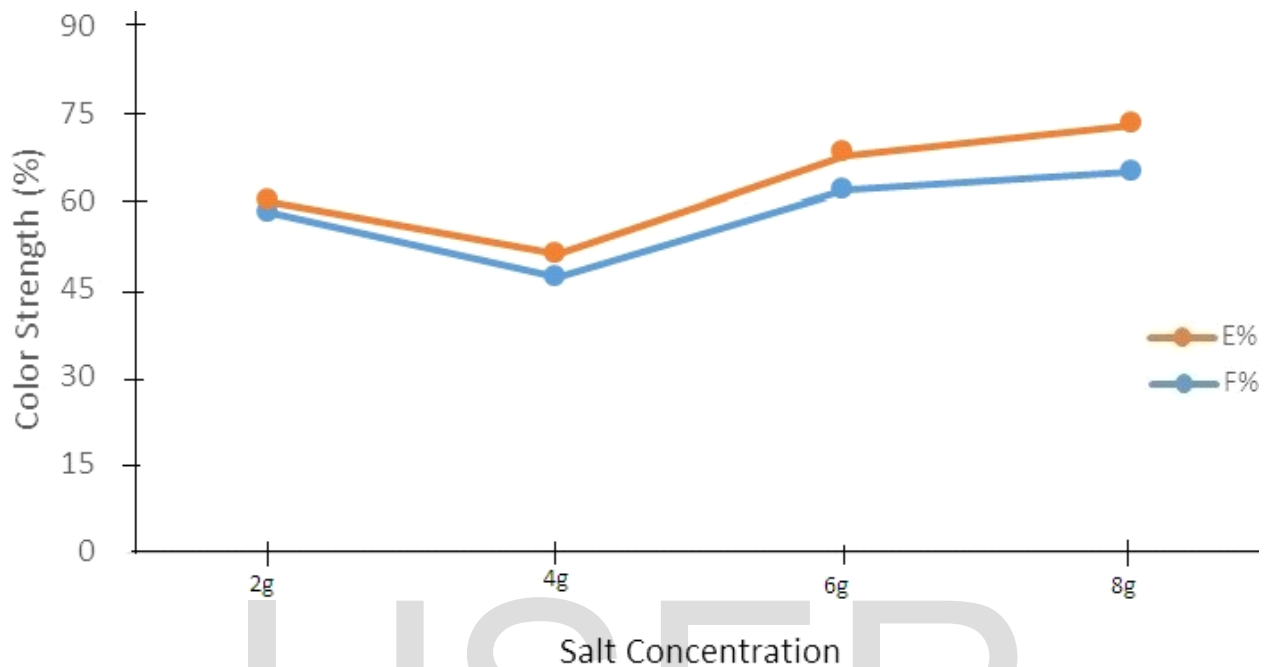


**Figure 3.2** Effect of % of exhaustion and % of fixation values at altered dyeing temperature for prepared direct dye.

### 3.3 Impact of salt concentration by exhaust shading

Salt anticipate that a fundamental part will impel the rate and stretch out of fumes shading. The results of shading quality utilizing different unions of salt were contemplated four stilbene base direct tints. Salt particle e.g. sodium chloride confines into  $\text{Na}^+$  and  $\text{Cl}^-$  particles in water and  $\text{Na}^+$  particles has slant to butcher the interface between shading particle and fiber outskirts which empower the rate of fatigue of shading to the fiber material. Other than  $\text{Na}^+$  particles effectively get related with water atoms and point of confinement the level of hydrolysis of shading moieties. To improve the response conditions for starting late merged fiber-organize shades, the impact of salt (Glauber's salt) in various fixations i.e. 2g, 4g, 6g and 8g were considered concerning the (%) shading qualities. The qualities acquired for cotton were looked the masterminded coordinate tones which laid out most over the top shading quality in degree of 65-75 %. Since the surplus use of electrolyte may perhaps make shading supreme which acknowledges bringing down of development rate and prompts un-level shading onto the surface? Most important retention (%) result was gotten for shading organized direct shading (74%) with salt social event of 8g in figure 3.3. The outcomes showed that little measure of salt (Glauber's salt) can be reasonable to get higher shading yield for the quick shading onto the pretreated cellulosic surface if there should be an occasion of fumes shading. Comparative

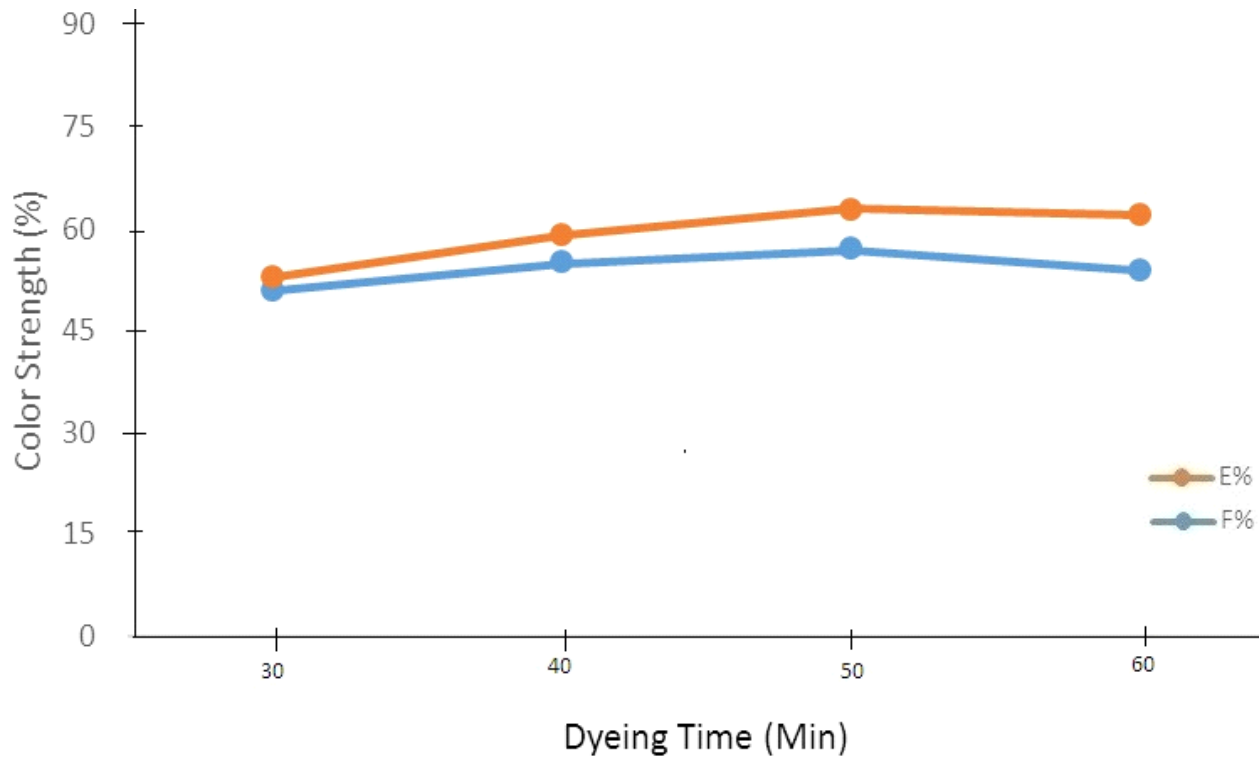
outcomes were additionally revealed in which they utilized sodium sulfate as electrolyte to the shading liquor of direct hues to develop the take-up of shading to pretreated surface.



**Figure 3.3** Effect of % of exhaustion and % of fixation values at altered sodium chloride concentration for prepared direct dye

### 3.4 Effect of shading time on shading nature of surfaces

Shading is the technique by which surfaces material are never-endingly shading with the shading reliably to get even shade and is done in watery medium when in doubt. Time is in like way a key parameter in influence the level of fatigue and last obsession of the provoke shading to cotton. The exhaust technique was utilized at separate shading time i.e. 30, 40, 50 and 60 minutes with a specific genuine target to complete the best shading quality on cotton. It associates with the spread of shading complete through the shading shower onto the cotton surface and into inside surfaces. There is an entry incline in exhaustion % E and fixation % F regards for orchestrated shading with shading time. The information acquire from vapor shading procedure for all tones .the best shading quality estimation of exhaustion % E are 78% for masterminded coordinate shading get at shading time that is 60 minutes.

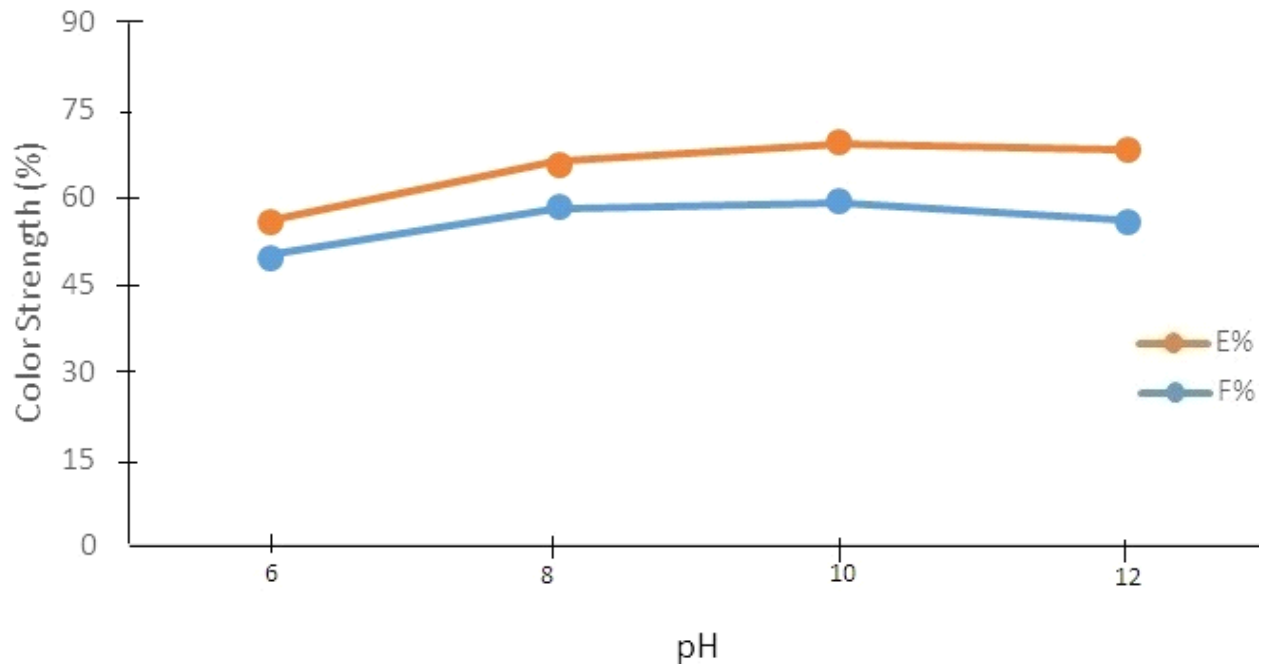


**Figure 3.4** Effect of % of exhaustion and % of fixation values at altered dyeing time for prepared direct dye.

### 3.5 Influence of pH on shading quality

Shading quality for the planned tints is also pH subordinate. The examination of shading quality for the stillbene based direct shading was advanced by picking grouped estimations of pH i.e. 6,8,10 and 12 autonomously. The outcomes which are uncovered in the figure 3.5 show that most over the top shading quality respect i.e. 78 % at pH of 12 proposed for orchestrated direct shading. Shading yield (%) reached out with the pH, which is a consequence of the way that the stillbene based direct dyes work better in dissolvable medium, which was in appreciation to the shading yield appeared by the responsive tints. Happens gotten by [11] showed high substantively rate to the cotton surface at high pH regards in perspective of bury atomic powers between the fast shading and fiber.





**Figure 3.5** Effect of % of exhaustion and % of fixation values at altered pH for prepared direct dye.

### 3.6 Fastness testing

Fastness tests were carried out by using standard techniques précised by American Association of Textile Chemists and Colourists and International Organization for Standardization (AATCC and ISO). The fastness test discussed as follows.

#### 3.6.1 Color fastness to crocking

Color fastness to dry and wet crocking was determined by utilizing ISO 105-X12 method. This test technique was designed to evaluate the amount of color from colored textile dyestuff through rubbing process. A test specimen (5 × 13 cm) of colored material was rubbed with white crock test cloth during wet and dry process under controlled conditions. The transferring of color to white cloth was compared with American Association of Textile Chemists and Colourists (AATCC) gray scale for stains. Then, a grade was assigned. Rating 5 stands for excellent and 1 for poor was assigned to each dyed fabric material. The range of Grey scale values for rubbing fastness is 1-5. The samples of rubbing tests are given in table 3.2.

### 3.6.2 Color fastness to light

Color fastness to light was demonstrated according to ISO 105-B02 test technique by using light fastness tester. Its color characteristic was checked in sunlight or artificial light source like mercury tungsten fluorescent bulb. Dyed fabric material (10 × 50 mm) to be tested was exposed at the same time to a source of light under specific conditions for 48 hours. The color fastness to light of test material was determined by evaluating the color change of exposed part to the unexpected original sample comparing with American Association of Textile Chemists and Colourists (AATCC) gray scale for color changing [12]. The range of Grey scale values for light fastness is 1-8. The samples are given in table 3.2.

### 3.6.3 Color fastness to washing

Color fastness to washing was determined by ISO 105-CO3 test technique by SDL Atlas (England) M228B Rota wash. Dyed fabric specimen of 0.5 g was stitched with multi fibre undyed white specimen. Then, the sample was set in the stainless steel glass container with 25 mL soap solution. The soap solution contained 2 g of anhydrous sodium carbonate per litre. Stainless steel glass container was heated to 60 °C for half an hour. Then, the sample was removed and rinsed with tap water. After it, it was dried. The color change in the dyed sample and fabric stains were determined with grey scale. Change of the shade and staining on the adjacent white fabric were watched. The range of Grey scale values for washing fastness is 1-5. The results of washing tests are given in table 3.2.

**Table 1.2** Fastness properties of synthesized dye on cotton fabric by exhaust dyeing process.

Fastness Property	Change of Shade	Staining on adjacent fabric
(1) Washing Fastness	4	4.5
(2) Rubbing Fastness	Rating of Dry Rubbing	Rating of wet Rubbing
	5	4
(3) Light Fastness	Grey Scale Value	
	5	

## Chapter-4

### Conclusion

Another 4,4-diamino biphenyl stillbene - 2,2 disulphonic destructive based direct shading had been set up through buildup of 4,4-diamino biphenyl stillbene-2, 2-disulphonic destructive with 2,4,6-trichloro-1,3,5-triazine and 1-amino-8-hydroxynaphthalene-3,6-disulphonic corrosive, diazotization of aniline and hydrolysis. In the wake of drying and grinding, it was hued on cotton surface. Hued cotton surface was depicted, for instance, light speed, rubbing speed, washing briskness. All the briskness properties for the prepared shading were in a respectable range 4-5. Effect of salt obsession incapacitate shading was moreover thought about. The most extraordinary ingestion % result was obtained for shading (74%) with salt concentration 8g. The effect of pH on shading moreover considered. The best shading quality was seen at 70 oC for shading 74%. The best shading quality regard was 78% at pH 12. The effect of kicking the pail temperature on shading quality was in like manner inspected. The most outrageous shading quality estimation of weariness gets at kicking the pail time 60 minutes. For the assurance and identification of qualities useful gathering recurrence of mixes, Fourier Transform infrared spectrometric efficient strategies were used. These all regards demonstrated the criticalness of the organized direct shading.

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