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“Synthesis, Characterization & Dyeing Properties of Bi-functional Reactive Dye “ Diazotized 5-(4- Methoxy Phenyl) -1,3-Thiazole-2- Amine-Cyanurated Naphthionic acid-Para Cresidine Vinyl Sulphone” ”.

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Abstract: Bi-functional reactive dyes are colored compounds that have more than one reactive moiety per molecule or groups, capable of forming covalent bonds between dye ions or molecules and the substrate. This bi-functional reactive dye was synthesized with S- Triazine and Vinyl Sulphone groups via 5-(4-Methoxy Phenyl)-1,3-Thiazole-2-Amine. This intermediate was diazotized, coupled with Cyanurated Naphthionic acid and other various Cyanurated coupling components to synthesize the such bi-functional reactive dyes by using PCVS and % exhaustion & % fixation of dyes were determined by using glauber salt as fixing agent at various temperature condition. Washing & light fastness were determined. The overall result concluded that methoxy group was introduced in para position of benzene ring has been induced for increasing substantivity & reactivity of dye molecule.

Key-words: Bi-functional, Covalent bond, % exhaustion, % fixation, fastness

Introduction:

Dye is a color organic compound which is used for imparting color to the substrates. Dye is a combination of chromophore and auxochrome. Dyes are classified into many classes on the basis of their application such as : (1) Acid dyes (2) Basic dyes (3) Direct dyes (4) Mordant dyes (5) Azoic dyes (6) Vat dyes (7) Sulphur dyes (8) Disperse dyes (9) Reactive dyes (10) Solvent dyes. The above dyes have many application but Reactive dyes find many applications in paints, inks, cosmetics, in dyeing various fibers

among all above dyes.

Reactive dye is a color organic compound which has suitable reactive group capable of forming a covalent bond between carbon atom of dye and oxygen, nitrogen and sulphur atom of -OH, -NH₂ and -SH groups, respectively of the substrate. Reactive dyes can be classified into different groups as follows:

(1) Reactive dyes containing Cyanuric chloride nucleus which is sub divided into (a) Mono-chloro triazine reactive systems (hot brand

reactive dyes) (b) Di-chloro triazine reactive systems (cold brand reactive dyes) classes.(2) Reactive dyes containing Chloro pyrimidine nucleus (3) Reactive dyes containing Chloro pyridazine nucleus (4) Reactive dyes containing Di-Chloro-Quinoxaline nucleus (5) Reactive dyes containing Vinyl Sulphone group (6) Reactive dyes containing Acrylamide group (7) Reactive dyes containing an Epoxy group. Various above reactive systems are known but cyanuric chloride (trichloro-triazene) and vinyl sulphone derivatives are widely used because the presence of 1,3,5 triazine structure in the dye molecules improves their dyeing ability and possibility for application.[1] and S-Triazine based chemicals have been widely used in manufacture of polymers, dyes, explosives, pesticides, and commodity chemicals.[2]

There are two reactive systems:

Mono-functional reactive systems:

These systems can react only once with the nucleophilic groups in the fiber. Examples are the Halo Triazine and Vinyl Sulphone systems. However, when one of the halogen atoms is replaced by reaction with other functional group in the fiber or with alkali in dye bath, the reactivity of the remaining halogens is decreased.[3] So dye-intermediates with one functional group have low degree of fixation. So to overcome this deficiency dye-intermediates with two or more functional groups have been synthesized.

Bi-functional reactive systems:

Bi-functional reactive dyes are colored compounds that have more than one reactive component per molecule or groups, capable of forming covalent bonds between dye ions and molecules or the substrate. Bi-functional reactive dyes classified into two types: [4]

Homo bi-functional reactive dyes: These dyes have two same reactive centers.

Hetero bi-functional reactive dyes: These dyes have two different reactive centers. However, reactive dye containing hetero bi-functional groups can provide great opportunity for dye-fiber reaction due to sulphatoethylsulphone and monochlorotriazinyl reactive systems.[5] From the azo chromophore, many dyes can be obtained by various different couplers, diazo components (Primary amines) and reactive systems. (Most widely used reactive systems are Cyanuric chloride (Trichloro-Triazene), and Vinyl Sulphone derivatives.) These dyes are known as Azo Reactive Dyes. Various coupling components (Such as, Amido Naphthol Sulphonic acid, Naphthyl Amine Sulphonic acid, etc.) can be used to synthesize the Azo Reactive dyes.[4, 6-7]

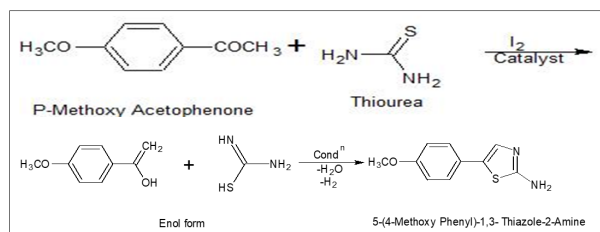
Materials & Methods - Experimental Procedure:

Dye-intermediates with one functional group have low degree of fixation. So to overcome this deficiency, dye-intermediates with two or more functional groups have been synthesized. This bi-functional reactive dye was synthesized with S- Triazine and Vinyl Sulphone groups via 5-(4-Methoxy Phenyl)-1,3 -Thiazole-2 -Amine intermediate in following 4 steps:

Step-1: Synthesis of 5-(4-Methoxy Phenyl)-1,3 - Thiazole-2 -Amine intermediate:

First 0.062 mole Iodine crystal, 0.100 mole 4-Methoxyacetophenone, & 0.13 mole Thiourea were taken in round bottom flask. Then the reaction mixture was heated in oil bath at 120-130°C for 5-6 hrs. Then the reaction mixture was cooled and it was diluted with 50-60 ml distilled water and was heated it until dissolve most of Solid. Then the reaction mixture was cooled and was treated with 6N NH₄OH (pH-8-

10).The Precipitates of above intermediate was collected and was purified by crystallization from hot ethanol.[8]



Step-2: Preparation of Naphthionic acid with Cyanuric chloride and PCVS [8]:

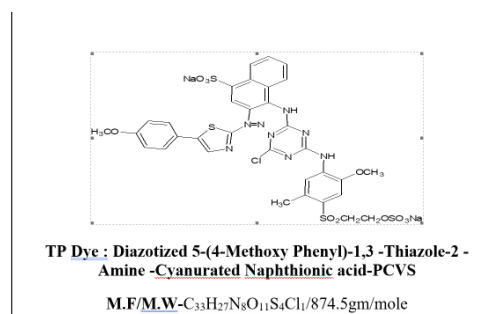
In this step, first 0.010 mole Cyanuric chloride was taken in round bottom flask. Then it was dissolved in 40 ml acetone and 10 ml distilled water. This solution was kept for 1 hour to form fine suspension at low temperature. After 1 hour, a solution of Naphthionic-acid (0.010 mole) in 10 % w/v HCl was added into the cyanuric chloride solution in such way that the temperature could not rise above 5 °C. The reaction mass was stirred up to 2 hours. Then, in another beaker Para Cresidine Vinyl Sulphone (0.005-0.006 mole) was added in 10 ml distilled water. This above solution was added into above reaction mass with constant stirring. The reaction-mixture was stirred for half an hour at 0-5 °C with gradually rising of temperature to 40 °C adjusting pH to 7.5. The mixture was stirred for 3-4 hours, and then filtered it, washed it with cold water and the resultant product was used for subsequent coupling reaction.

Step-3: Diazotization of 5-(4-Methoxy Phenyl)-1,3-Thiazole-2-Amine :

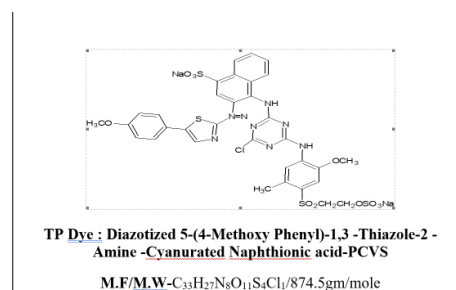
The diazotization was carried out by direct method. In a 250ml beaker, 0.010-0.020 mole of 5-(4-Methoxy Phenyl)-1,3-Thiazole-2-Amine, 0.015 mole of Na₂CO₃ and 50 ml of water were taken. The solution was warmed until the clear solution was obtained. The reaction mixture was placed in ice bath to cool at 0-5 °C. Now cold

the solution of 0.020 mole of NaNO₂ into 5 ml of water was added into the cold solution of above 5-(4-Methoxy Phenyl)-1,3-Thiazole-2-Amine solution slowly with constant stirring. Now, this solution was poured with stirring into 500 ml beaker containing 5 ml concentrated H₂SO₄ and crushed ice. This mixture was stirred well for 10 minutes and maintaining the temperature below 10 °C.

Step-4: General method of coupling [8]:

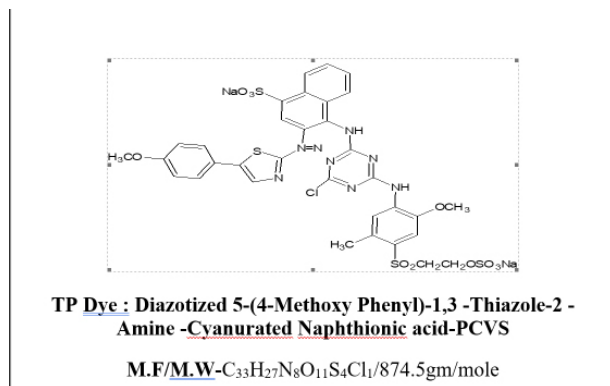


The Coupling compound (Preparation was given in Step-2) (0.0050- 0.01 mole) was stirred in 2.5-3 ml water at 0-5 °C. The diazonium sulphate



solution of above intermediate 5-(4-Methoxy Phenyl)-1,3-Thiazole-2-Amine was added over 1 hour maintaining the pH at 7.0. The stirring was continued for 4 hours at 0-5 °C. A solution of Na₂HPO₄ (0.0008-0.0009 mole) and KH₂PO₄ (0.0001-0.0002 mole) in 2 ml water followed by sufficient amount of NaCl (0.08-0.09 mole) was added to the precipitates of the product. Organic impurities were extracted by washing with small portion of ethyl alcohol.

Structure of Diazotized 5-(4-Methoxy Phenyl)-1,3 -Thiazole-2 - Amine -Cyanurated Naphthionic acid-PCVS



Materials & Methods- Dyeing of fabrics and Dyeing properties:

Dyeing Performance was done by two method: (1) Digital weighing balance method (2) Optical Density (OD) measurements by spectrophotometer (**Model - COLOREYE 7000A, Company name- AGS NOVASCAN**) The dyeing of this synthesized bi-functional reactive dye was done by Glauber salt method. The dye bath (**Model- ROTA DYER (water-bath), Company name- RBENG, Mumbai**) was adjusted to pH at 9.0. The dyeing was allowed for 1 hour at 80°C.[9] Then aqueous solution of a synthesized dye(0.5-1.0 gm) was prepared with 25 ml distilled water and then initial and final OD of dye solution was determined.

% Exhaustion of Synthesized Dyes:

% Exhaustion was determined by Optical density measurements with the help of spectrophotometer. Then From the value of initial and final OD of dye solution, % exhaustion was determined.

$$\% \text{ Exhaustion} = \frac{\text{Initial OD} - \text{Final OD}}{\text{Initial OD}} \times 100$$

Where OD= Absorbance **OR** Optical density

Initial OD = Values before dyeing Final OD = values after dyeing

% Fixation of Synthesized Dyes:

% Fixation was calculated using this equation.
 $\% \text{ Fixation} = 100 - \% \text{ Exhaustion}$
 At the end, the tested dyed sample was used for determining fastness properties upon cotton and wool.

Determination of fastness properties:

These are the properties of dyes which indicate tolerance of dyes on the fiber towards the action of various foreign agencies, like, light, washing, heat (sublimation), rubbing, perspiration, etc. The dyed samples were tested by using standard methods: Different color fastness test has been given adequate results with the help of grayscale. The fastness properties of synthesized dye was observed at pH 12 and 70 °C

Color fastness to washing:

The dyed sample was stitched between cotton and wool fibers. Then specimen was immersed into aqueous solution of soap- non-ionic detergent, and then sample was removed and rinsed two times in hot and cold water. Then the results were determined by using gray scale method.

Color fastness to light:

The dyed fabric was exposed to light for 24 hrs. Then the results were determined by using gray scale method.

Gray Scale Range and its Significance:

The light fastness of synthesized dyes show range of 1-8 in gray scale method.[10] 1 indicates low light fastness and 8 indicates excellent light fastness. The washing fastness of synthesized

dyes show range of 1-5 in gray scale method. [10] 1 indicates low washing fastness and 5 indicates excellent washing fastness.

Result & Discussion-Characterization:

This Synthesized bi-functional reactive dye was characterized by IR analysis by using Shimadzu FTIR-8400S With DRS spectrometer by using pressed pellet technique. From the IR analysis we can say that The results of IR analysis were matched very well with standard values of various functional groups [11].

(IR(Cm⁻¹): -OCH₃: 1240.27, C₆H₅OCH₃: 1469.81, -SO₂CH₂CH₂OSO₃Na: 1002.25, 1305.55, -CH₃: 3030.27, -N=N: 2060.40, : 1046.25).

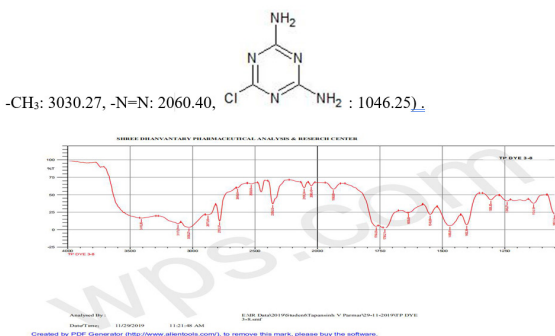


Fig -1: The Result of IR analysis

This Synthesized bi-functional reactive dye was characterized by NMR analysis by using 400 MHz liquid state NMR spectrometer in DMSO - d₆ solvent for detecting different kinds of protons present in dye molecule (Model-Bruker 400 MHz FT- NMR Spectrometer with 5 mm BBO Pro behead). The results were inferred according to standard values. [12,13] (NMR(δ): 2.513(S,1H, -NH), 2.10(S,3H, -OCH₃ & -CH₃), 0.132(S,2H,-CH₂), 11.187(m, 4H & 5H, Aromatic ring proton), 4.400(S,1H, Thiazole ring proton)).

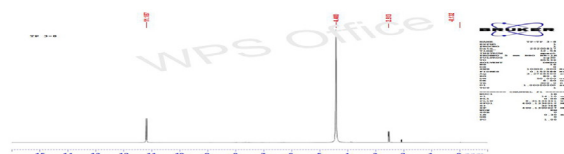
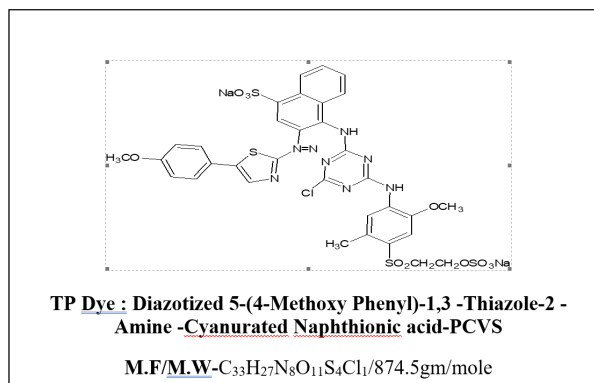
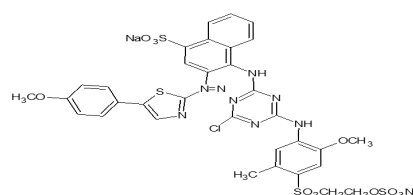
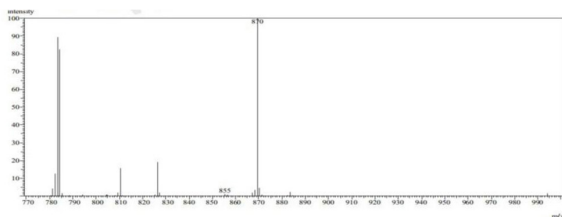


Fig-2: The Results of NMR analysis

At the end synthesized bi-functional reactive dye was characterized by mass analysis[11] using Shimadzu GC - MS QP-2010 Ultra Mass Spectrometer in CDCl₃ solvent. From the mass spectra we can say that The m/e value is very well matched with the value of molecular weight.

Mass Spectrum of TP Dye





MS (m/e): 870

Fig -3: The Result of Mass analysis

Results & Discussions- Shadings:

The synthesized dye give bright color of visible region. Here shadings of this synthesized bi-functional reactive dye are given in table-1.

Results & Discussions- Dyeing Performance:

Then the results of % Exhaustion and % fixation values of synthesized dye are given in following table-2.

TABLE-2: Results of % Exhaustion and % Fixation values of synthesized dye.

No.	TP Dye on Cotton		TP Dye on Wool	
	% Exhaustion	% Fixation	% Exhaustion	% Fixation
1	7.98	92.02	9.96	90.04

Table-1: Structure and Shadings of synthesized dye on cotton and wool.

TP Dye& M.W.(gm/mole)	Structure of TP Dye	Shading on cotton	Shading on wool
<p>TP Dye Diazotized 5-(4-Methoxy Phenyl)-1,3 -Thiazole-2 - Amine- Cyanurated Naphthionic acid- PCVS 874.5</p>		<p>Bright Yellow</p>	<p>Bright Yellow</p>

From the results of % exhaustion and % fixations we can say that this synthesized bi-functional reactive dye show excellent and good affinity towards cotton and wool fabric.[14]

Result & Discussion- Fastness Properties:

The results of fastness property of various synthesized dye are given in following table-3.

TABLE-3: Results of Wash Fastness and Light Fastness of Synthesized Dye according to Gray Scale.

Period of weeks	Wash fastness		Light Fastness	
	Cotton	Wool	Cotton	Wool
1	5	5	5	5
2	4-5	4-5	4-5	4-5
3	4-5	4-5	4-5	4-5
4	4	4	4	4
5	4	4	4	4

Here, from the results of washing and light fastness of synthesized dye, we can see that synthesized dye show 4-5 range in gray scale method. It indicates that these synthesized dye has been shown excellent to washing fastness and moderate to light fastness.

Conclusion:

This new bi-functional reactive dye containing two reactive groups, which was synthesized easily and has been shown to have wide range of bright shades.(Bright Yellow). Due to formation of Diazotized Methoxy Phenyl Thiazole Amine (Chromophore/Chromogens) having Cyanurated Naphthionic acid (Auxochrome) in combination with Para Cresidine Vinyl Sulphone derivative and so that this dye achieved bright shade (Bright Yellow) at various reactivity levels.

From the results of % exhaustion and % fixation (Table-2) of synthesized dye, it is clear that this synthesized bi-functional reactive dye Diazotized 5-(4-Methoxy Phenyl)-1,3-Thiazole-2-Amine-Cyanurated Naphthionic acid- PCVS show excellent and good affinity towards cotton and wool fabrics.

This bi-functional reactive dye synthesized from 2 -Amino Thiazole has been synthesized easily and shown to have good dyeing performance upon cotton and wool. Different color fastness test has been given adequate results with the help of grayscale. The fastness properties of dye was observed at 4-5 range on gray scale at pH 12 and 70 °C. The results proved that the fastness on cotton and wool has been excellent to washing and moderate to light.

Methoxy group was introduced in thiazole moiety has been induced for increasing substantivity and reactivity of dye. This synthesized bi-functional reactive dye have thiazole moiety with chlorotriazine and PCVS nucleus. Due to methoxy group in Vinyl Sulphone, it increases reactivity towards fiber and thus it achieves high degree of fixation

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