# Thermalstability and Photostability of new Azo dye

Hana,a Kadhem Egzar , Noor Mustafa Kamal, Hana,a Adii Ali , and Muthana Saleh Mashkour

Department of Chemistry, Science College, University of Kufa, Najaf, Iraq

**Abstract-** In this work Azo dye {(2,2-(3,3-dimethylbiphenyl-4,4-diyl) bis (1-(2-hydrazinyl-3,5-dinitrophenyl)diazene)} have been prepared and characterized by, spectorphotometric method UV-Vis, FT-IR spectrum and <sup>1</sup>H-NMR spectrum. The absorption maxima was observed in the 464 nm, Thermogravimetric(TG) and differential scanning calorimetry (DSC) of this compound was measured, The photostability of azo dye in water occurred under UV irradiation processes. Dyeing process has on the dye prepared it gave good results. we have found that the colors of cotton fabrics after dyeing was orange

*Index Terms*- azo dye; Thermostability; Photostability

#### I. INTRODUCTION

S ynthetic dyes are broadly used in paper printing, fabric dyeing, food, medicines, color photography, cosmetics and other manufacture  $^{(1)}$ .

Azo dyes are one of the very consequential and multilateral classify artifical organic compounds, with an immense variety of using  $^{(2,3)}$ . Azo dyes which calcalate for 60 - 80% of the dyes consumed in fabric tretment  $^{(4,5)}$  are distinct by a typical double azo bond linkage (-N=N-), which is the most

frequent chromophore of azo dyes. Usually azo dyes have azo linkages between one to three, linking naphthyl rings or phenyl that are Usually substituted with some of functional groups for instance sulphonate, triazine amino, nitro, methyl, hydroxyl and chloro <sup>(6)</sup>.

Thermal analysis plays an major role in the study of the stability and structure of dyes. The application of some dyes for specific the thermal stabilities of them are also very important(7). The resistance to

uses and detect heat at elevated temperatures is one of the main properties required of dyes used in high temperature processes such as dyeing, printing and photocopying and in high technology areas for instance lasers and electro optical devices(8).

The complex light-induced fading method of azo dyes corresponds to

various factors and their chemical structures foroever play the most consequential role (9-13).

Light fastness is an important factor in the determination of the useful life span of textiles. Light may produce two different fibrous materials; on the one hand the colour can fade, on the other hand

changes in dyed photochemical degradation of the fibrous material can take place. (14)

Many factors effect the photostability of dyes, and these principally contain the chemical structure of the dye, The dye physical state on the fibre, the substrate chemical structure of, additives within the substrate, composition of atmospheric (water,oxygen and contaminants), temperature of the ambient and the spectral distribution of the incident light.<sup>(15)</sup>

We report here the synthesis, photostability, thermostabilities and application of new azo dye on cotton fabrics.

# **Chemical and Instruments**

All chemicals used in this study were supplied from different internationl companies such as Merch, Fluke and BDH chemicals company, including; O-tolidine, 2-4dinitrophnyl hydrazin, ethanol, sodium hydroxide, and distilled water. The synthesized azo dye was subjected to infrared spectra were acquired KBr disc technique by using infrared SHEMADZU FT.IR-8400S and <sup>1</sup>HNMR.

## Experimental procedures of Synthesis of azo dye

O-tolidine (2.12 g, 0.01mol) was dissolved in (3.5 ml) of concentrated HCl and (40 ml) D.W. The mixture was cooled at (-5C°) ice — water bath. Asolution of sodium nitrite (1.72 g, 0.02 mol) dissolved

in (6 ml) of D.W , there was added adropwise to the mixture with stirring. In the other beaker 2-4 DNPH (2.96 g, 0.02 mol) dissolved in (1.32 g) of NaOH dissolved in (44ml) of D.W and place this beaker in ice-water bath

at (-5C°). The cold diazonum chloride was added to the coupling agent in small portions and stirred after each addition, Acompleting the addition, the reaction mixture was stirred less than (0C°) for (15) minutes. The black end result was precipitated and filtered recrystallized from ethanol yiled(2,2'-(3,3'-dimethylbiphenyl-4,4'-diyl)bis(1-(2-hydrazinyl-3,5-dinitrophenyl)diazene)

Schem (1) step of preparation of azo dye

# Photostability experimental procedures

Samples of dye solution was irradiated with a UV source for 10,20, 30, 40, 50,60, 70, 80,90 and 100 min, in this experiments conducted in the photoreactor with a circulation water at 298±2 K,

 $_{
m that}$   $_{
m were}$  during process of the light irradiation . A 200 mL of dye solution  $_{
m that}$  was  $_{
m placed}$  into the reaction container. At 10 min intervals, about 2 mL dye solution was collected and the UV-vis absorption ranging from 200 nm to

800 nm was measured using UV- Spectrophotometer . The decoloration  $_{\rm proportion~of~azo~dye~was}$  calculated by the following formula:

(Decoloration (%) =  $(A_0-A)/A_0 \times 100\%$ )

where A and  $A_0$  are the residual and initial absprption of dye solution each in order.

#### Dyeing experimental procedures

In this research we have been dyeing cotton tissue by dye prepared, according to dyeing azo dye way (Azotic Dyes) which called dyeing snow and are in accordance with the following steps:

- 1- Prepare raw cotton tissue through the removal of starch, good boiling and bleaching.
- 2- Dissolve the dye: dye prepared dissolved in 10 ml of ethanol and 0.2 ml of sodium hydroxide and then complete the volume to 150 ml with distilled water at pH equal to 10.
- 3- Gmarat raw cotton in the soda for 30 minutes in a water bath containing 0.0004M sodium nitrite solution and 0.9 ml of HCl acid and 150 ml of distilled water in 15-20 ° C. Then raw dried degree normal temperature
- 4- put the cotton tissue in the bathroom of the display, which contains 0.1 g of dye and 1 ml of sodium hydroxide concentration of 0.32 M and continue treatment for 30 minutes in temperature 10- 15. Oevdil use of ice as it is obtained is usually the best results at low temperatures.
- 5- Washed raw in a soap bath and sodium carbonate to remove the dyeing materials outstanding Bavh for true color And thereby improve the stability force against the light, washing and friction, then removed the soap solution by rinsing process, a washing with cold water and dried

# Resulte and discusion

The new prepared dye known to be one of thermal and photo stable materials (18)

The chemical structure of the dye  $2,2^{-}(3,3^{-}$ -dimethylbiphenyl- $4,4^{-}$ -diyl)bis(1-(2-hydrazinyl-3,5-dinitrophenyl) diazene was determine by FT-IR, <sup>1</sup>HNMR, and UV-Vis spectra. UV-Vis absorption spectra of dye solution was registered in methanol, the absorption maxima( $\lambda$  max) of dye was found in 464 nm fig. 2.

FT-IR fig. (3) which showed appearance bands at (1598-1543) cm<sup>-1</sup> of stretching vibration of two (N=N) groups. Stretching vibration of (C-H) of alkyl group in o- tolidine appear at (2904)cm<sup>-1</sup>, the appearance band at (3417-3277) cm<sup>-1</sup> stretching vibration of two hydrazone -NH groups, the band at (1234) cm<sup>-1</sup> stretching vibration of (N-N) groups.

The <sup>1</sup>H-NMR spectra signals at 2.8 ppm due to the existence of methyl groups in o- tolidine in the compound, signals (7.2-7.8) ppm due to aromatic protons of new compound , 8.5 ppm (hydrazone NH). These signals depict more characteristic prove for the formation of this compound fig(4).

Direct irradiated under ultraviolet (UV) light alone of dye solution shown in Fig. 5. The efficiency of degradation of dye solution was calculated to be 5.771% at 100 minuts by using  $1\times10^{-4}$ M concentration of dye solution .

These results show that much better stable for the dye under UV irradiation was occur when the azo solution was irradiated by UV light

only. The values of the efficiency of degradation after irradiation for the<sub>difference times increases with time,</sub> especially after 100 min,indicating that the photostability of dye is usually accepted (15) that the photooxidation of azo dyes consist of attack by photochemically create

singlet oxygen<sup>(16)</sup>.the photostability can be personal quality to the auxochromes which mean electron-withdrawing or electron-donating substituents that make more acute in color of the chromophore by altering

the total energy of the electron system for each dye<sup>(17)</sup>.

Thermal stability that was measured and represented in Figure 6. It shows that the dye started decomposing at  $290^{\circ}$ C and its weight losing was 68.27% up to the temperature studied  $(600^{\circ}$ C), and this showed that the sample dye has thermal stability up to  $290^{\circ}$ C. And photooxidation process shown photostability for dye.

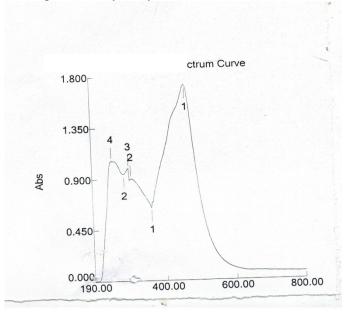


Fig. (2): UV-Vis absorption spectra of dve

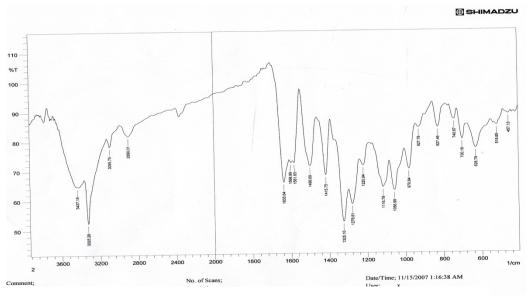


Fig.(3): FT ¬IR spectra of dye

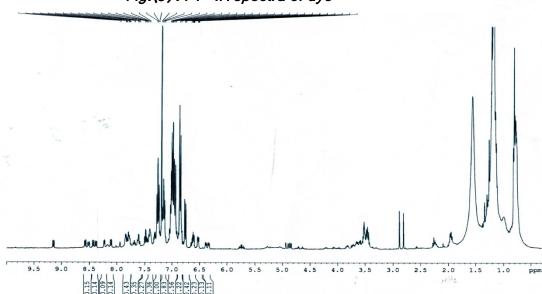


Fig. (4): HNMR-spectra of dye

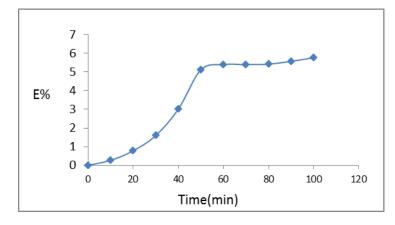


Figure 5. The efficiency of degradation of dye at differant

From Figure.6 it is shown that the weight losses observed between 50-150  $C^{\circ}$ , 150-290  $C^{\circ}$  and 290-600  $C^{\circ}$ . The temperature limits (50-150  $C^{\circ}$ ) is assigned to the loss of hydrate water, and the other

vary within values are refer to the decomposition stages of dye. From the TG curves in Figure 6, the weight change were 7.187%, 68.27% and 23.53% at a heating rate 10°C/min.

The DSC curve of dye gives two endothermic peaks at 75 C°which mention to dehydrate of water and at 230 C $^{\circ}$  this endothermic peak corresponding to melting of compound at 230 C $^{\circ}$ , the DSC curve shows exothermic peak at 600 C $^{\circ}$ . This information propose that the thermal stability of the dye.

consequently, the TG and DSC studies on dye showed that they can

be used for many uses applications in types fields like as fabric fibres, that need thermal stability until to 150 C°.

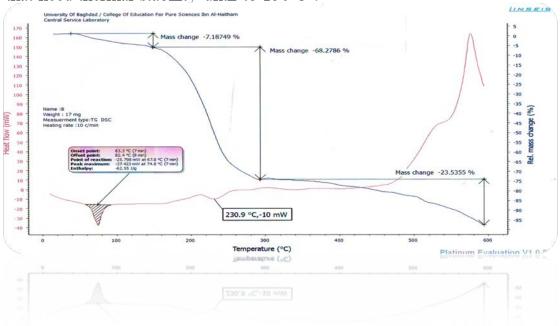


Fig. (6): TG and DSC curve of dye

Dyeing process has on the dye prepared dyeing process has in the acidic environment and has adopted a method of the snow dyeing, which is concerned with azo dyes only Because being prepared at low temperatures insatiable seersucker alkaline solution has been subjecting the samples dyed with dyes prepared a series of tests that usually take place after the pigments applied to cotton fabrics for the purpose of evaluation. The most important of these tests, the extent of resistance to sunlight and laundry detergents and color stability (20). As it gave good results, we have found that the colors of cotton fabrics after dyeing was orange.

## II. CONCLUSIONS

The azo dye was synthesized by diazotisation- coupling and oxidation reactions in good yield shows greatly better photostability beneath UV irradiation and thermostability, it  $\lambda$ max was observed at 464 nm .The decomposition temperatures of dye was found to be in the range 290–600 C°. The dye was better stable when the dye under UV irradiation, consequently, the thermal and photo stability studies on dye showed that

can be used for versatile applications in several fields which require photo and thermal stability. Dyeing process has on the dye prepared it gave good results. we have found that the colors of cotton fabrics after dyeing was orange

#### REFERENCES

- [1] Rafi, F., Franklin, W. and Cerniglia, C.E. (1990). azoreductase activity of anaerobic bacteria isolated from human intestinal microflora. Appl. Environ. Microbiol., 56:2146-2151.
- [2] Natansohn, A.; Rochon, P., Chem. Rev., 2002, 102, 4139; Natansohn, A.; Rochon, P. In Photoreactive Organic Thin Films; Sekkat, Z.; Knoll, W. eds., Academic Press: Amsterdam, 2002, p. 400.

- [3] Rau, H. In Photochemistry and Photophysics; Rabeck, J.F. ed., CRC Press Inc.: Boca Raton, 1990, 2, 119; Rau, H., In Photoreactive Organic Thin Films; Sekkat, Z.; Knoll, W.eds., Academic Press: Amsterdam, 2002, p.3.
- [4] Mendez-Paz, D., Omil, F., and Lema, J.M. (2004). Anaerobic treatment of azo dye Acid Orange 7 under batch conditions. Enzy. Microbial. Technol. 36: 264 272
- [5] Yang, Q., Yediler, A., Yang, M., and Kettrup, A. (2004). Decolourisation of an azo dye reactive black 5 and MnP production by yeast isolate: Debaryomyces polymorphus.Biochem. Eng. J. 24: 249 253.
- [6] Bell, J. Plumb, J.J., Buckley, C.A. and Stuckey, D.C. (2000) Treatment and decolourisation of dyes in an anaerobic baffled reactor. J. Environ. Eng. 126 (11): 1026-1032.
- [7] M.S. Masaund, E.A. Khalil, E. El-Sayed El Shereafy and S.A. El-Enein, J. Thermal Anal., 36, 1033 (1990).
- [8] R. Egli, (1991). Color Chemistry The Desing and Synthesis of Organic Dyes and Pigments, ed. A.T. Peters, H.S. Freeman, Elsevier, London,
- [9] T Hihara; Y Okada; Z Morita. Dyes Pigments, 2004, 60(1), 23-48.
- [10] D Zhuang; L Zhang; D Pan; J. He. Color. Technol., 2007, 123(2), 80-85.
- [11] SN Batchelor; D Carr; CE Coleman; L Fairelough; A Jarvis. Dyes Pigments, 2003, 59(3), 269-275.
- [12] Zs Csepregi; P Aranyosi; I Rusznák; L Töke; J Frankl; A Víg. Dyes Pigments, 1998, 37(1), 1-14.
- [13] G. Kricsevskz kij and J. Gombkoto. (1975) Sretostokkosty okrasennih tek stilnih Izdelij, Legkaja Indutria Moskva.
- [14] Kazimierz Blus Technical University of Lodz Institute of Polymers and Dyes Technology Żeromskiego 116, 90-543 Lodz, Poland FIBRES & TEXTILES in Eastern Europe January / December 2005, Vol. 13, , 6, 54.
- [15] H. Zhan, H. Tian, Dyes Pigments 37 (1998) 231.
- [16] (a) P. Desai, E. Couthino, J. Mol. Struct. (Theochem), 528 (2000) 29;(b) S. Tauro, E. Couthino, J. Mol. Struct. 532 (2000) 23.
- [17] Safwat Mohammad Abdul Azeez Saleh, "HPLC Determination of Four Textile Dyes and Studying Their Degradation Using Spectrophotometric Technique"2005, An-Najah National University Faculty of Graduate Studies.
- [18] zollinger. H, colour chemistry: synthisies, properties and applications of organic dyes and pigments, (Wiley-VCH),2003,P 187.
- [19] J.Martin and E,Blackburn; J.Chem. Education, 77 (2000) 935.
- [20] L.Fedorov, M.Zhukov and A.Ermakov; Izv. Akad. Nauk. SSSR, Ser.Khim, (1984) 1185.

#### **AUTHORS**

First Author – Hana,a Kadhem Egzar, Department of Chemistry, Science College, University of Kufa, Najaf, Iraq Second Author – Noor Mustafa Kamal, Department of Chemistry, Science College, University of Kufa, Najaf, Iraq Third Author – Hana,a Adii Ali, Department of Chemistry, Science College, University of Kufa, Najaf, Iraq Fourth Author – Muthana Saleh Mashkour, Department of Chemistry, Science College, University of Kufa, Najaf, Iraq