

Research Article

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Synthesis of Direct dyes based on non-carcinogenic amines for leather and textile industry

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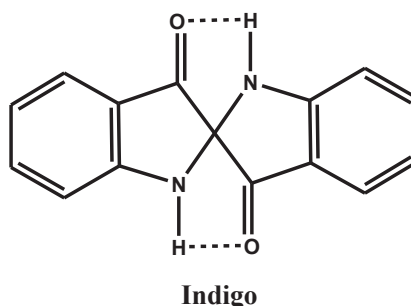
ABSTRACT: A series of direct dyes based on 4,4'-diaminodiphenylamine-2'-sulphonic acid (**1-5**) have been synthesized to be used as potential alternative to benzidine (human carcinogenic) and they are eco-friendly. Benzidine derivatives containing alkoxy groups ortho to an amino group of meta-phenyl diamine removed carcinogenicity. The Benzidine analogue was diazotized and coupled with widely used dye intermediate dye like FC acid to generate a group of direct dyes giving yellow, mustard, blue, purple and greenish black shades on cotton, leather and wool. Dye structures were confirmed by visible absorption spectra, IR spectra, and fastness property. Dye purity was confirmed by TLC using BuOH: EtOH: NH₄OH:H₂O (3:1:0.5:1) as the fluent. The dyed fabrics showed very good to excellent wash fastness and moderate to good light and perspiration fastness properties.

Key Words: Benzidine, azo dye, direct dyes, Coupling reaction, diazotization; H-acid; FC-acid, J-acid, electronic spectra, cotton, leather, fastness.

INTRODUCTION

Prehistorical man has already dyed furs, textile and other objects with natural substance mainly of vegetables, but also of animal origin e.g. dyes such as Indigo was derived from natural sources (indigofera tinctoria, a native plant of Asia). Alizarin was obtained from madder wood, while others such as Azo dyes and direct dyes which are meant for specific applications are obtained

by synthesis [1].



The first synthetic dye Picric acid was obtained by treating indigo with nitric acid

was subsequently used for dyeing silk as yellow

1.1 Classification of Dyes

The dyes have been classified according to their chemical constitution or method of application [2-7].

According to constitution dyes may be

- i) Homocyclic (mainly include nitro, nitroso, azo, triphenyl methane, pyrazolone, anthraquinone and phthalin)
- ii) Heterocyclic (mainly includes formazans and Eosin)

According to applications dyes may be

- i) Acid dyes (picric acid and methyl orange)
- ii) Basic dyes (triphenyl methane)
- iii) Direct dyes (congo-red)
- iv) Mordant dyes (Alizarin)
- v) Vat dyes (indigo blue and white)
- vi) Ingrain Dyes (nitro aniline)
- vii) Sulphur dyes (methylene blue)
- viii) Reactive dyes (1,3,5-Triazine)
- ix) Solvent dyes
- x) Disperse dyes (dispersal fast red)

Azo dyestuffs are considered to be

one of the largest chemical groups of dyes presently in existence and their success is due to simple synthetic procedures involved, the great structural diversity of available compounds, generally high molar extinction coefficients and medium to high fastness properties with respect to both light and wetness. [8-10]. There are several ways for describing in scientific terms the characteristics of a particular colour. When colour is assessed on the basis of reflectance measurements, it is common to consider the three relevant attributes of perception of colour as hue, Chroma and lightness [11]. In addition, the disposal of toxic dye effluents containing azo dyes has raised public concern and attention to their environmental damage on aquatic life owing to their 104 carcinogenic nature, as well as inhibition of sunlight into the water stream, which impedes the photosynthesis process of aquatic plants and eventually causes an imbalance in our ecosystem [12-17]. The presence of dyes in effluents is a major concern due to their adverse effects to many forms of life. The discharge of dyes in the environment is a matter of concern for both toxicological and aesthetic reasons. Industries such as dye synthesis, printing, paper, textile, leather, electroplating, pulp mill, plastics, food and cosmetics, all use dyes in order to colour their products and simultaneously consume substantial volumes of water [18-23]. Dyes are of complex aromatic molecular structures and are stable towards heat and oxidizing agent. It has been reported that most industrial dyes are non-biodegradable, chemically stable, carcinogenic and mutagenic, hence, harmful

to human health. Several dyes are toxic to flora and fauna, and therefore pose health hazard. Moreover, presence of industrial dyes in water bodies also decreases light penetration which affects the photochemical activities of marine systems. Therefore, effective treatment of wastewater effluents from these industries via removing the dyes in order to meet regulatory requirement for reuse or discharge is highly desirable [24]. Many methods have been developed in the decoloration process, such as adsorption, reverse osmosis, precipitation and ion exchange. Identification of pigments and dyes is one of the most important targets aimed at the scientific examination of paintings, textiles, illuminated manuscripts and other historical and archaeological materials. Several analytical techniques have been used for this purpose, for example gas chromatography/mass spectrometry, UV-visible spectrophotometry, thin-layer chromatography, high-performance liquid chromatography, reversed phase liquid chromatography and capillary electrophoresis with electrospray mass spectrometric detection, FT-IR spectroscopy and Raman spectroscopy[25].

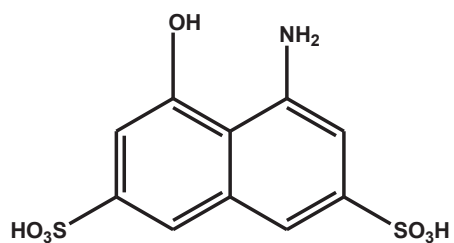
EXPERIMENTAL

All solvents and reagents were obtained from commercial sources. The purity of the products was carried by thin-layer chromatography (TLC) Melting points were determined by the open capillary method. The dyes were characterized by

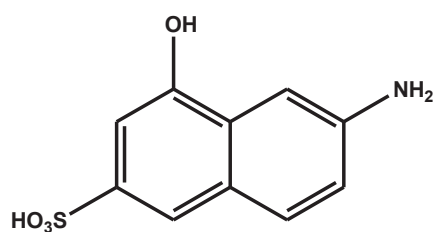
visible absorption spectroscopy using Unicam SP 800 spectrophotometer, IR spectral bands obtained from Pekin Elmer 100 FT-IR spectrophotometer.

General procedure

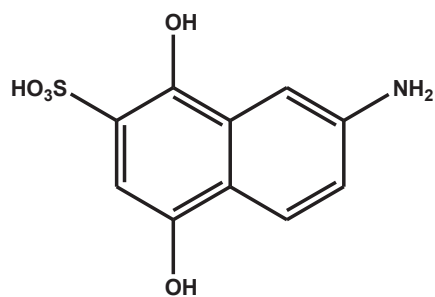
The synthesis of dyes (**1-5**) involved three steps in the first step diazotization (scheme 1) takes place. 4,4'-Diaminodiphenylamine-2'-sulphonic acid was dissolved in distilled water, the concentrated HCl was added. The mixture was stirred for 2hours, placed in the ice bath at 0-5°C. NaNO₂ solution was added. The contents of the flask was Checked for the presence of acid with Congo-red, starch-iodide paper was used to test nitrite. The mixture was stirred for complete diazotization. The sulfamic acid was added to remove the excess nitrite. In the second step coupling reaction was carried out. Acid was dissolved in 100ml distilled water and 10% NaOH solution .the pH was maintained 8-9.The stirred diazotized solution (step one) was added to coupled solution (step two) to prepare tetrazo compound. A clear solution is obtained. In the third step, heated the solution at 50°C ,with the addition of 50g sodium chloride, precipitated, filtered the solution under suction, dried at 70-75°C.A solid crude dye (36.1g) is obtained. The purification is done by thin layer chromatography [26-27].



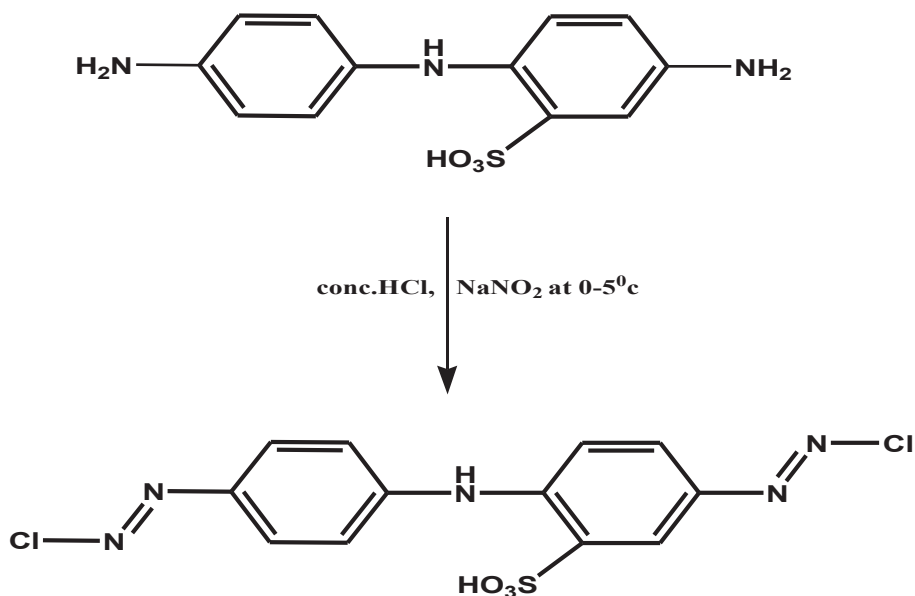
H-acid



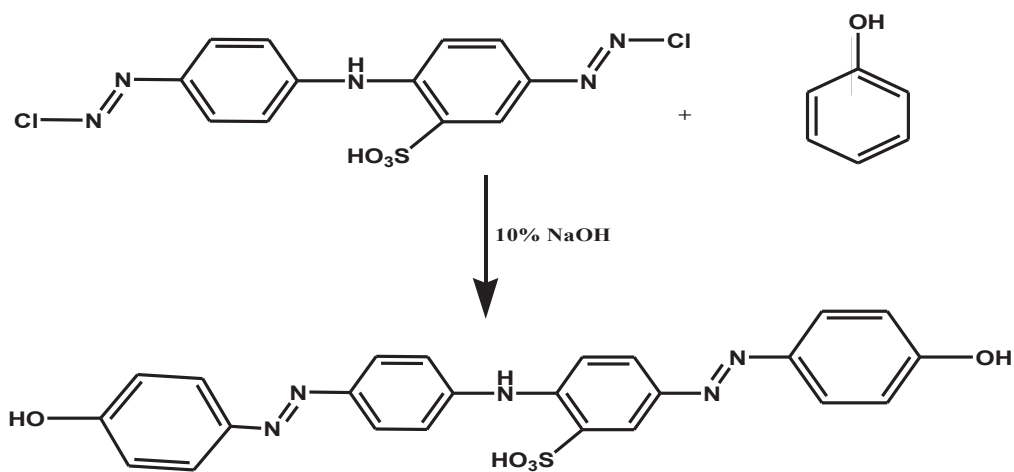
J-acid



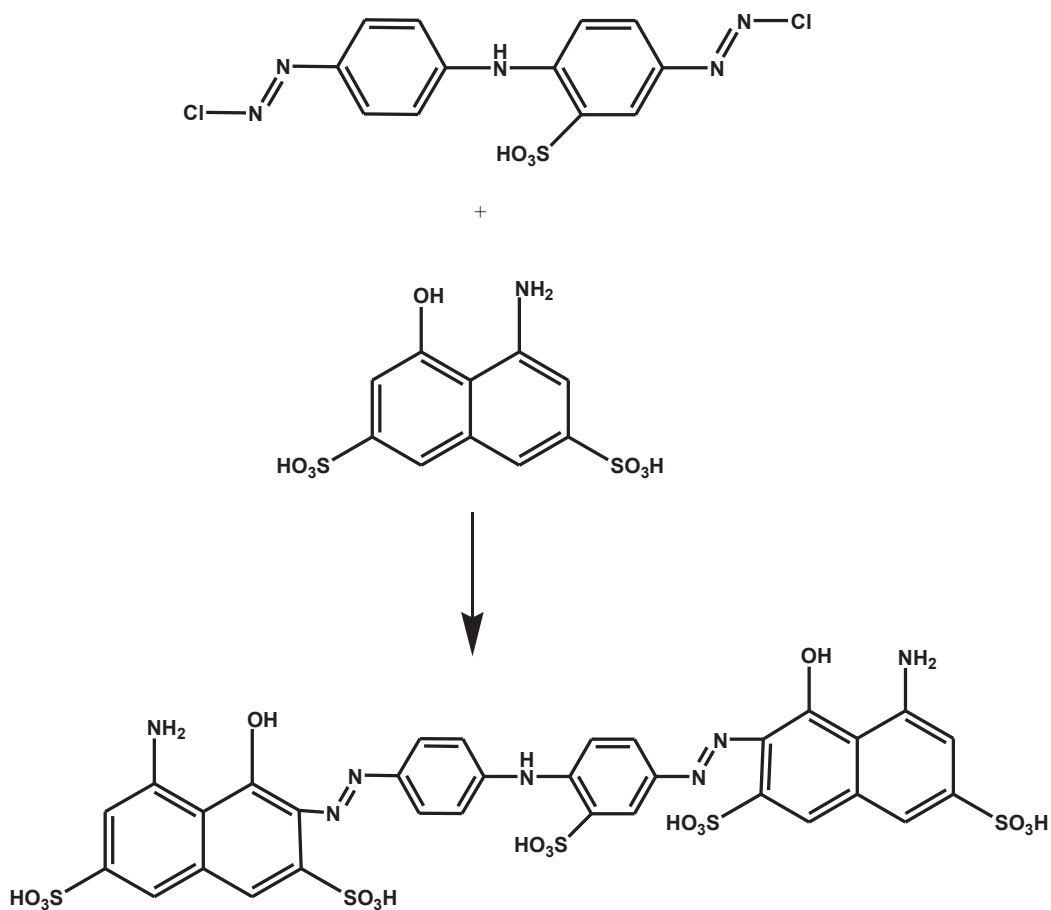
r-acid



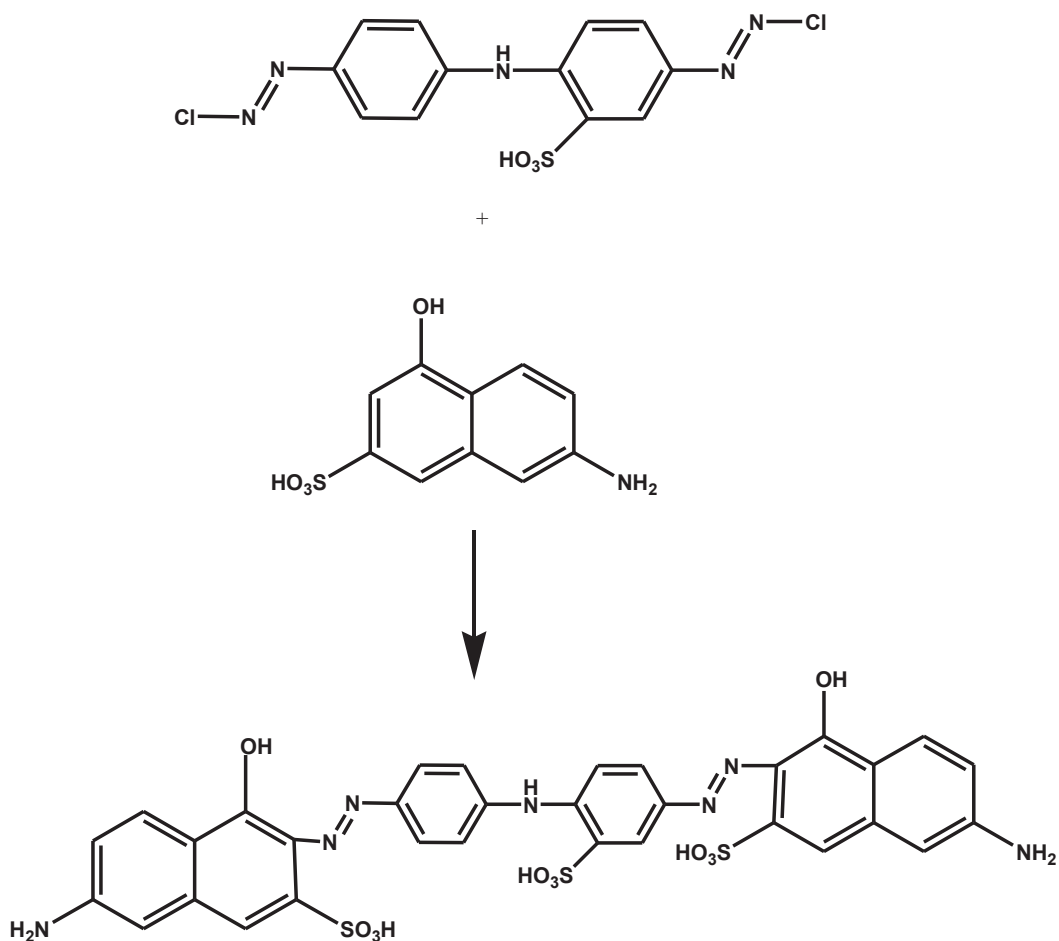
2.2 Synthesis of 4,4'-diazodiphenylamine-2'-sulphonic acid



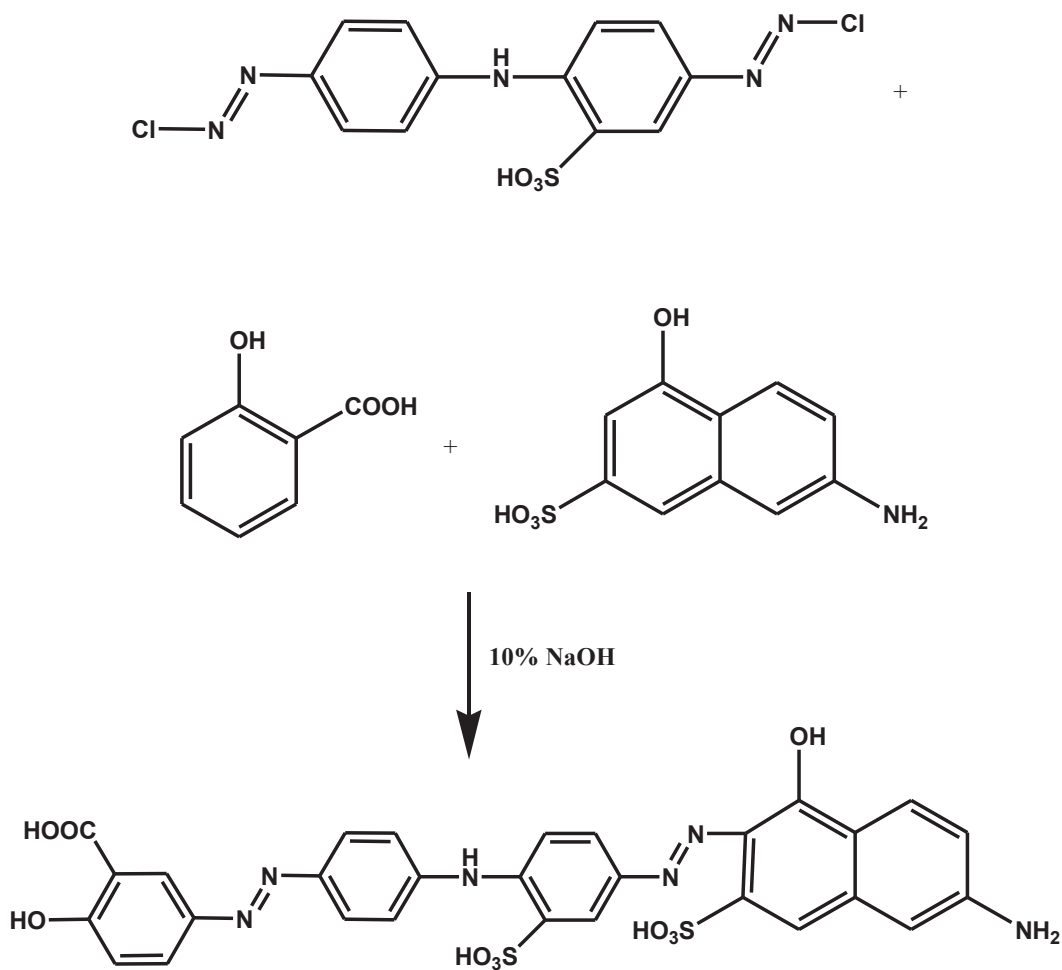
2.2.1 Synthesis of 4,4'-[di(p-hydroxybenzene)]diazodiphenylamine-2'-sulphonic acid



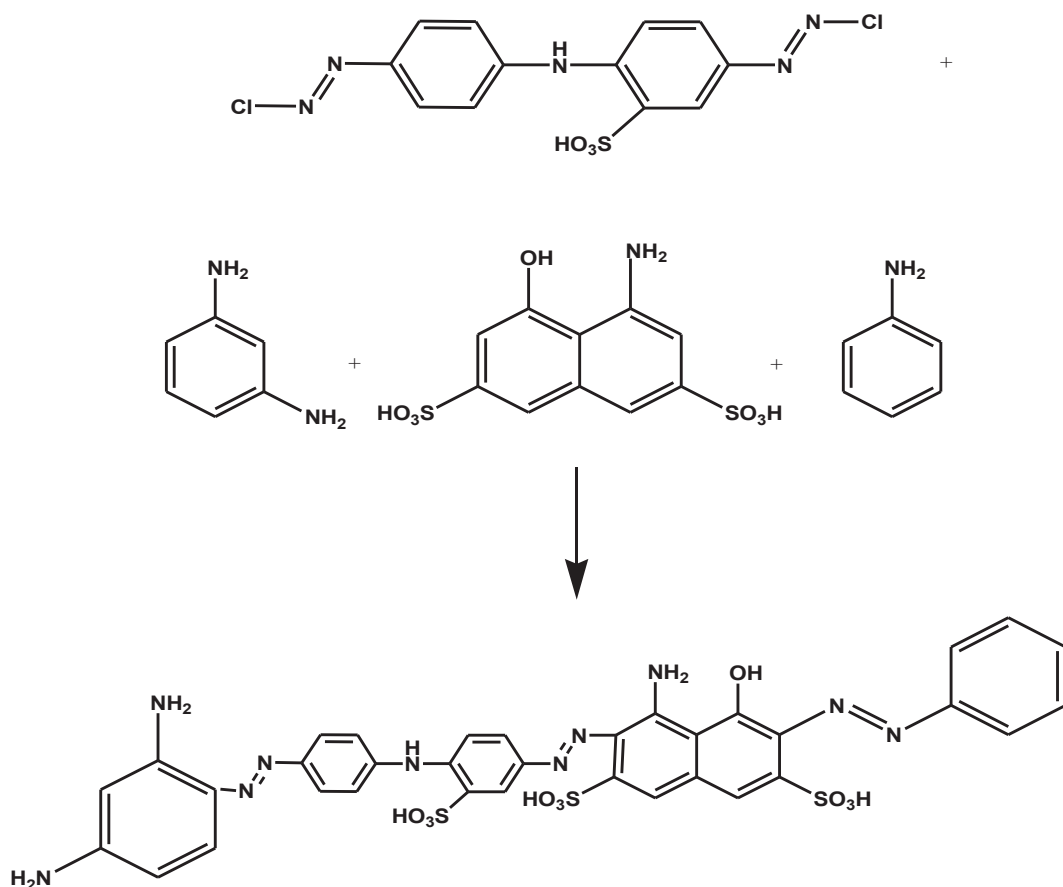
2.2.2 Synthesis of 4,4'-[di(1-hydroxy-3,6-disulfonic-8-aminonaphthalene)] diazodiphenylamine-2'-sulphonic acid



2.2.3 Synthesis of 4,4'-[di(1-hydroxy-4-amino-7-sulphonic naphthalene)] diazodiphenylamine-2'-sulphonic acid



2.2.4 Synthesis of 4 (4-hydroxy-3-carboxylic benzene), 4'-(1-hydroxy-3-sulfonic-6-amino naphthalene) diazodiphenylamine-2'-sulphonic acid



2.2.5 Synthesis of 4, [1,3-diamino benzene] 4'-1-amino-3,6-disulphonic-7-azobenzene-8-hydroxy naphthalene]-diazodiphenylamine-2'-sulphonic acid

DYEING

10g of goat leather were wet in the dyeing vessel for 4 hours containing 100 ml of water and 0.5ml of ammonia solution. The leather piece was then dyed for two hours at 55°C. in a fresh bath was set with 50ml of water 05 ml of ammonia and 1.5g of the direct shades(3%).near the end of dyeing,1ml of 85% formic acid was slowly added to exhaust the bath, stirred for two hours. Then removed

the dyed leather piece was squeezed, rinsed and dried in shade at room temperature, A level color was obtained.

The cotton cloth to be dyed, was first washed and dried.0.2g of dye was dissolved in 20-30 ml water and dipped in the stock solution. sodium chloride solution is added, kept the temperature near boiling. Dyeing duration was for 60-80min, So that cotton absorbed all the dye.

RESULT AND DISCUSSION

Direct dyes have been utilized to color cellulose for over 100 years. On account of their simplicity of use. In the mid 1970s the significant dyestuff is fabricated from benzidine-inferred dyes(genotoxic). The present research activity is an endeavor in this connection to replace benzidine derived asymmetric dyes with 4,4'-diaminodiphenylamine-2-sulphonic

acid.(a non-genotoxic).These direct dyes were synthesized by regular procedure of tetrazotization conc. HCL and NaNO₂ at 0-5 C taken after by the nearness of coupling with different couplers at indicated conditions. The yields of the items were in the scope of 70-85% .The colors were filtered and their dissolving focuses were recorded. Colors deteriorated at higher temperature >200-300C.

Table 1. Spectral data

Dye no.	Diazo compound	Coupling compounds	Shades of the dye	λ max.(nm)
1	4,4'-diaminodiphenylamine-2-sulphoni acid	Phenols	mustard	430
2	4,4'-diaminodiphenylamine-2-sulphoni acid	J-acid	purple	560
3	4,4'-diaminodiphenylamine-2-sulphoni acid	H-acid	blue	590
4	4,4'-diaminodiphenylamine-2-sulphoni acid	Salicylic acid & J-acid	brown	440
5	4,4'-diaminodiphenylamine-2-sulphoni acid	H-acid & aniline & m-diamino benzene	Greenish black	450

Table 2. Fastness properties

Sr.#	Fastness Test	Grey scale rating				
		D-1	D-2	D-3	D-4	D-5
1	Fastness to washing	4-5	4-5	4-5	4-5	4-5
2	Fastness to light	4-5	4-5	4-5	3-4	4-5
3	Fastness to hot pressing	4-5	3-4	4-5	3-4	4-5
4	Fastness to wet rubbing	3-4	3-4	2-3	3-4	4-5
5	Fastness to spotting acid	3-4	4-5	4-5	4-5	4-5
6	Fastness to spotting alkali	4-5	4-5	3-4	4-5	4-5
7	Fastness to dry rubbing	4-5	4-5	4-5	4-5	4-5

CONCLUSION

4,4'-diaminodiphenylamine-2'-sulphonic acid can be used to prepare direct dyes having comparable colours and fastness characteristics to commercial direct dyes. All the dyes **(1-5)** 4,4'-diaminodiphenylamine-2'-sulphonic acid proved to be an excellent replacement for carcinogenic benzidine-based direct dyes. The direct dyes **(1-5)** have brilliant shading quality and are eco-friendly. However, optimization of reaction conditions (pH and temperature) leads to the improved results. It is imperative that the findings of present research activity be exploited on semi pilot plant or industrial scale. So that more potential of these dyes on wool, cotton and leather to be explored.

REFERENCES

1. Arun Prasad AS, Bhaskara Rao KV (2010). Physico chemical characterization of textile effluent and screening for dye decolorizing bacteria. *Global J. Biotech. Biochem.* 5: 80-86.
2. Bafana A, Devi SS, Chakrabarti T (2011). Azo dyes: past, present and the future. *Environmental Reviews*. 19: 350–370.
3. Ben Mansour H, Houas I, Montassar F, Ghedira K, Barillier D, Mosrati R, ChekirGhedira L (2012). Alteration of in vitro and acute in vivo toxicity of textile dyeing wastewater after chemical and biological remediation. *Environmental science and pollution research international* DOI

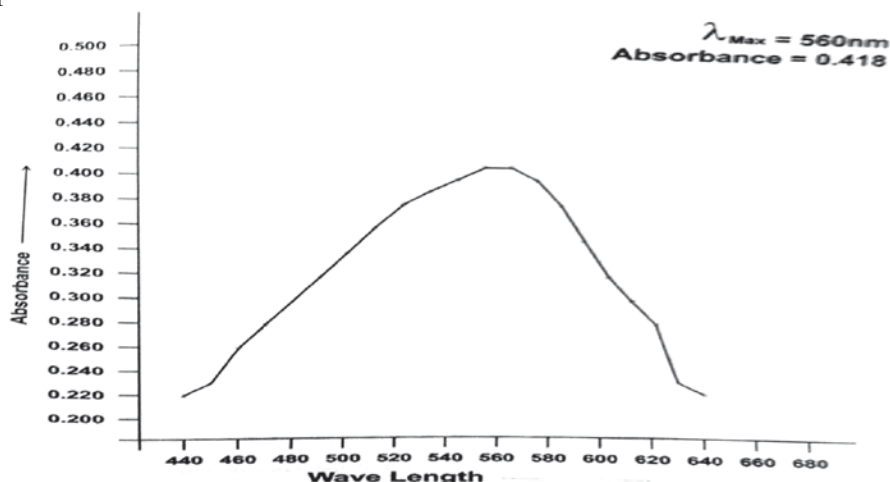
- 10.1007/s11356-012-0802-7.
4. Carneiro PA, Nogueira RFP, Zanoni, MVB (2007). Homogeneous photodegradation of C.I. Reactive Blue 4 using a photo-Fenton process under artificial and solar irradiation. *Dyes and Pigments*. 74: 127-132.
5. Couto SR (2009). Dye removal by immobilised fungi. *Biotechnol. Advan.* 27: 227-235.
6. Dos Santos AB (2005). Reductive Decolourisation of Dyes by Thermophilic Anaerobic Granular Sludge. PhD-Thesis. Wageningen University. Netherlands.
7. Dos Santos AB, Cervantes FJ, van Lier JB (2007). Review paper on current technologies for decolourisation of textile wastewaters: Perspectives for anaerobic biotechnology. *Bio-res. Technol.* 98: 2369-2385.
8. Forgacs E, Cserh ti T, Oros G (2004). Removal of synthetic dyes from wastewaters: a review. *Environ. Int.* 30: 953-971.
9. Ishegbe E, Bello KA, Kogo AA (2014). Synthesis and Application of Direct Dyes Derived From Terephthalic and Isophthalic Acids on Cotton Fabrics. *J. Polym. Tex. Eng.* 1: 50-58.
10. Kirk O (1979). *Encyclopedia of Chemical Technology*. 3rd ed, New York: Wiley-Inter Science.1: 167-172.
11. Kirk O (2004). *Encyclopedia of Chemical Technology*. v. 7, 5th Edition. Wiley-Inter- science.
12. Lee KM, Abdul hamid SB, Lai CW (2015). Multivariate analysis of photocatalytic mineralization of Eriochrome Black T dye using ZnO catalyst and UV irradiation. *Mater. Sci. Semicond. Process.* 39: 40–48.
13. Liu T, Li Y, Du Q, Sun J, Jiao Y, Yang G, Wang Z, Xia Y, Zhang W, Wang K, Zhu H, Wu D (2012). Adsorption of methylene blue from aqueous solution by graphene. *Colloids Surfaces B Biointerfaces*. 90: 197–203.
14. Nafisur AK, Rahman HR (2012). Studies on the Development of Spectrophotometric Method for the Determination of Quim. 35: 392–397.
15. Ogugbue CJ, Sawidis T (2011). Bioremediation and Detoxification of Synthetic Wastewater Containing Triarylmethane Dyes by *Aeromonas hydrophila* Isolated from Industrial Effluent. *Biotechnol. Res. Int.* DOI 10.4061/2011/967925. 168 Eco-Friendly Textile Dyeing and Finishing.

16. Pathania D, Sharma A, Siddiq ZMI (2016). Removal of congo red dye from aqueous system using Phoenix dactylifera seeds. *J. Mol. Liq.* 219: 359–367.
17. Perkins WS (1991). A Review of Textile Dyeing Processes. *ASTCC.* 23: 133-148.
18. Przysaś W, Zabłocka-Godlewska E, Grabińska-Sota E (2012). Biological Removal of Azo and Triphenylmethane Dyes and Toxicity of Process By-Products. *Water Air Soil Pol. Int.* 223: 1581-1592.
19. Rafatullah M, Sulaiman O, Hashim R, Ahmad A (2010). Adsorption of methylene blue on low-cost adsorbents: A review. *J. Hazard. Mater.* 177: 70–80.
20. Robinson T, McMullan G, Marchant R, Nigam P (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technol.* 77: 247-255.
21. Schwenecke H, Mayer D (2005). Benzidine and benzidine derivatives, *Ullmann's Encyclopedia of industrial chemistry*. Weinheim. Wiley. 101-104.
22. Sen S, Demirel GN (2003). Anaerobic treatment of real textile wastewater with a fluidized bed reactor. *Water Res.* 37: 1868-1878.
23. Silva CE, Silva LP, Edwards HGM. De oliveira LFC (2006). Diffuse reflection FTIR spectral database of dyes and pigments. *Anal. Bioanal. Chem.* 386: 2183–2191.
24. Wojciechowski K, Szadowski J (2003). Direct dyes derived from terephthalic and isophthalic acid. *Dyes and Pigment.* 56: 99-100.
25. Yaneva ZL, Georgieva NV (2012). Insights into Congo Red Adsorption on AgroIndustrial Materials - Spectral, Equilibrium, Kinetic, Thermodynamic, Dynamic and Desorption Studies. *A Review*, 4: 127–146.
26. Zollinger H (1987). Synthesis, Properties of Organic Dyes and Pigments. In: *Color Chemistry*. New York, USA: VCH Publishers: 92-102.
27. Zubair M, Jarrah N, Manzar MS, Al-harhi M, Daud M, Mu'azu ND, Haladu S (2017). Adsorption of eriochrome black T from aqueous phase on MgAl-, CoAl- and NiFe- calcined layered double hydroxides: Kinetic, equilibrium and thermodynamic studies. *J. Mol. Liq.* 230: 344–352.

Supporting information

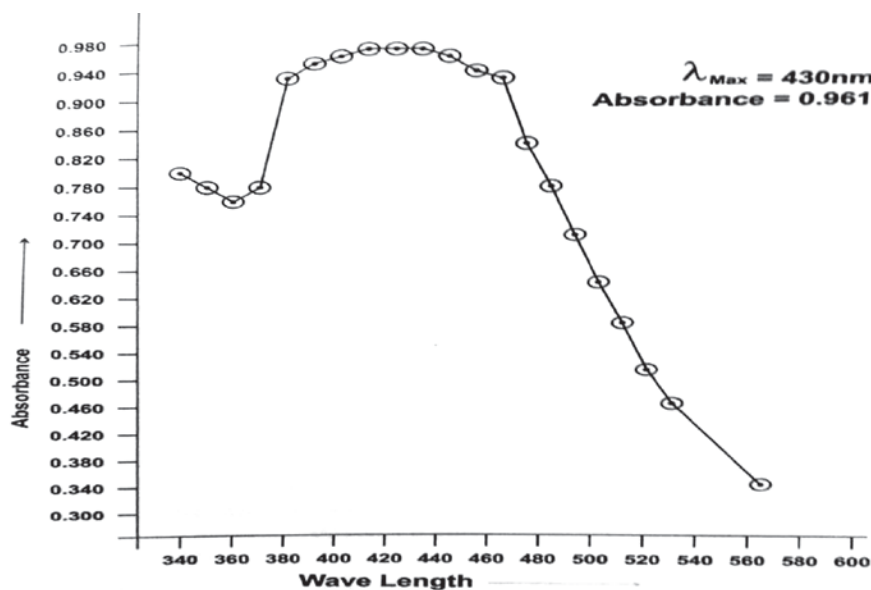
UV-Scan

DYE-1



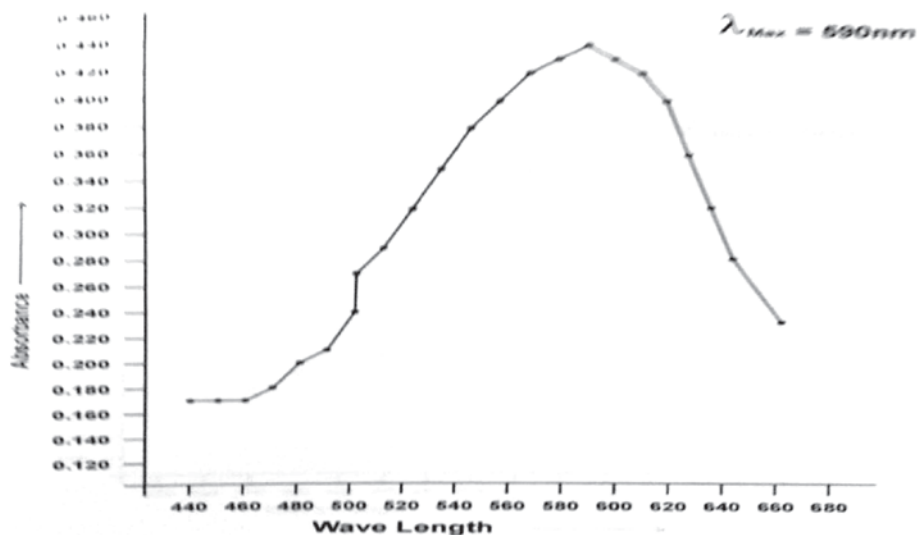
GRAPH #. 1

DYE-2



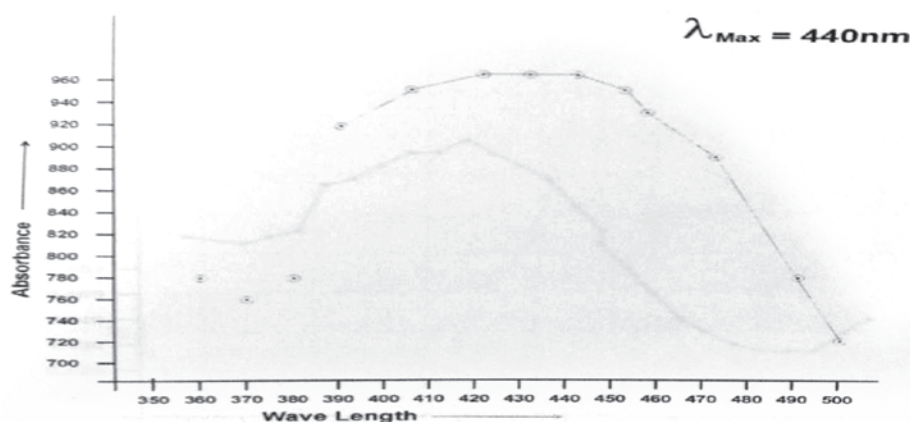
GRAPH #. 2

DYE-3



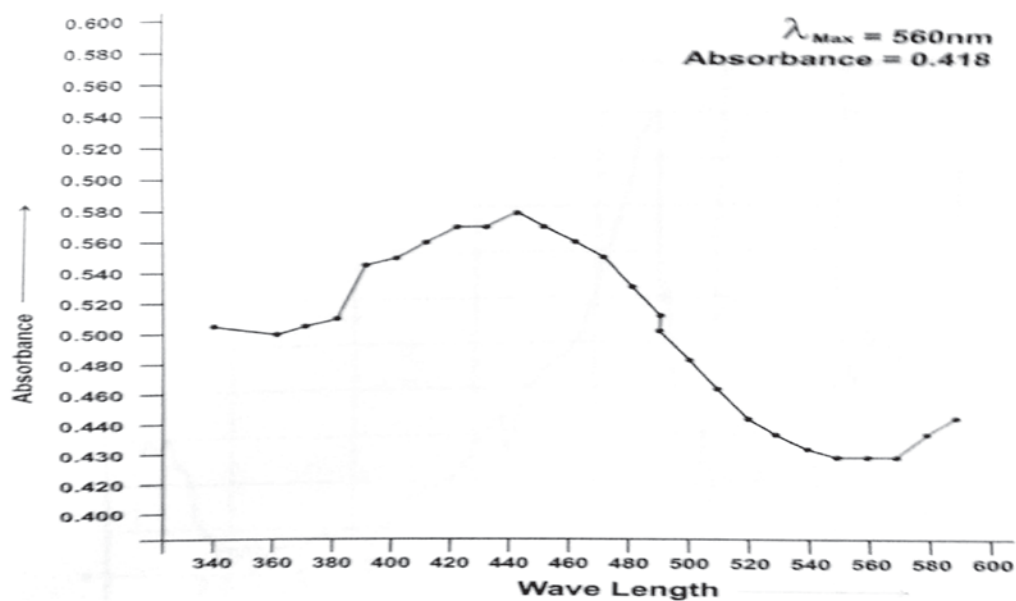
GRAPH #. 3

DYE-4



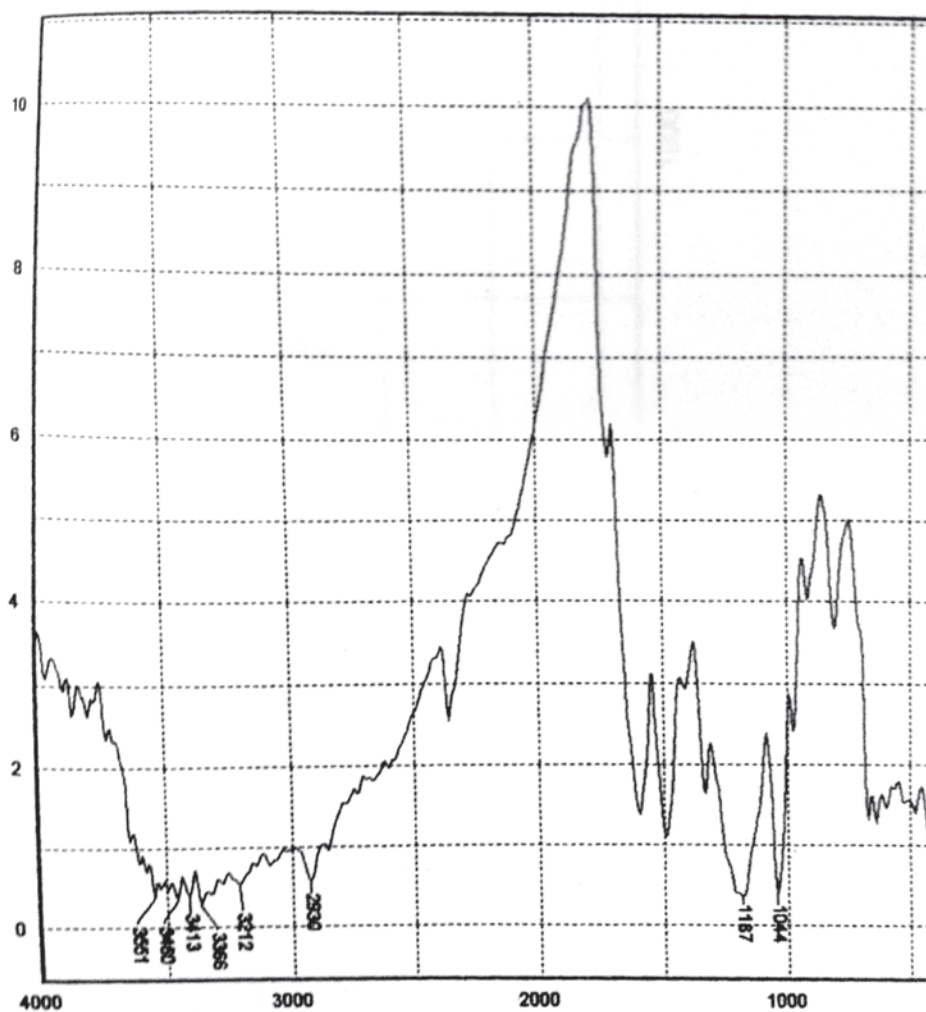
GRAPH #. 4

DYE-5

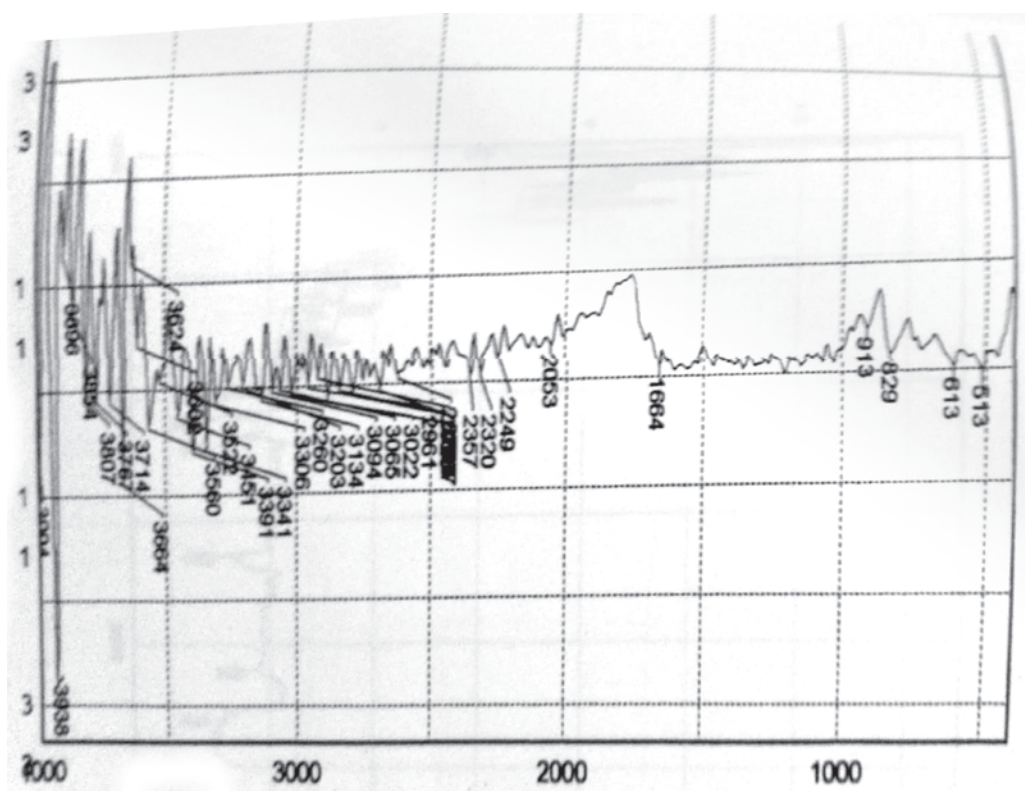


GRAPH #. 5

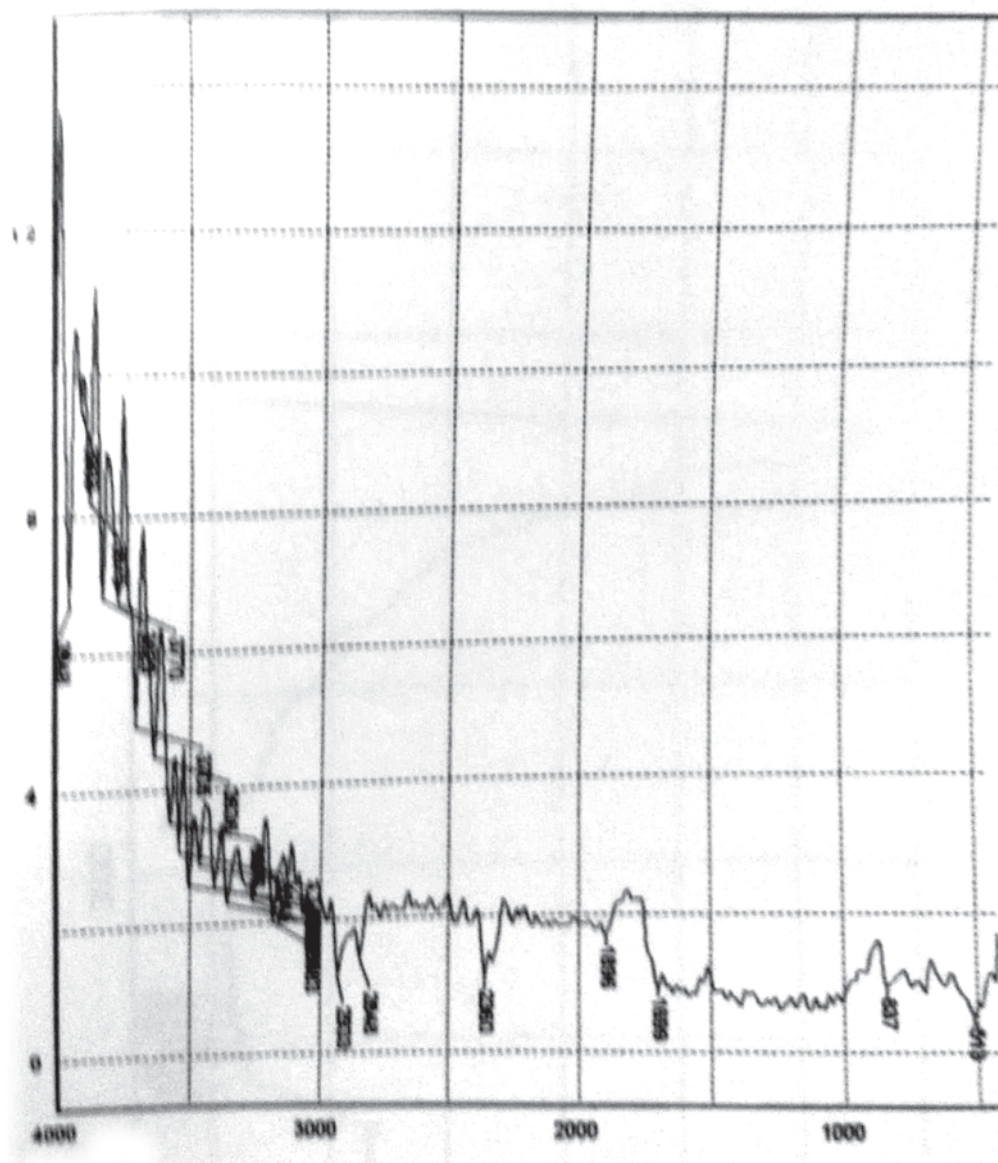
FTIR SCAN
DYE-1



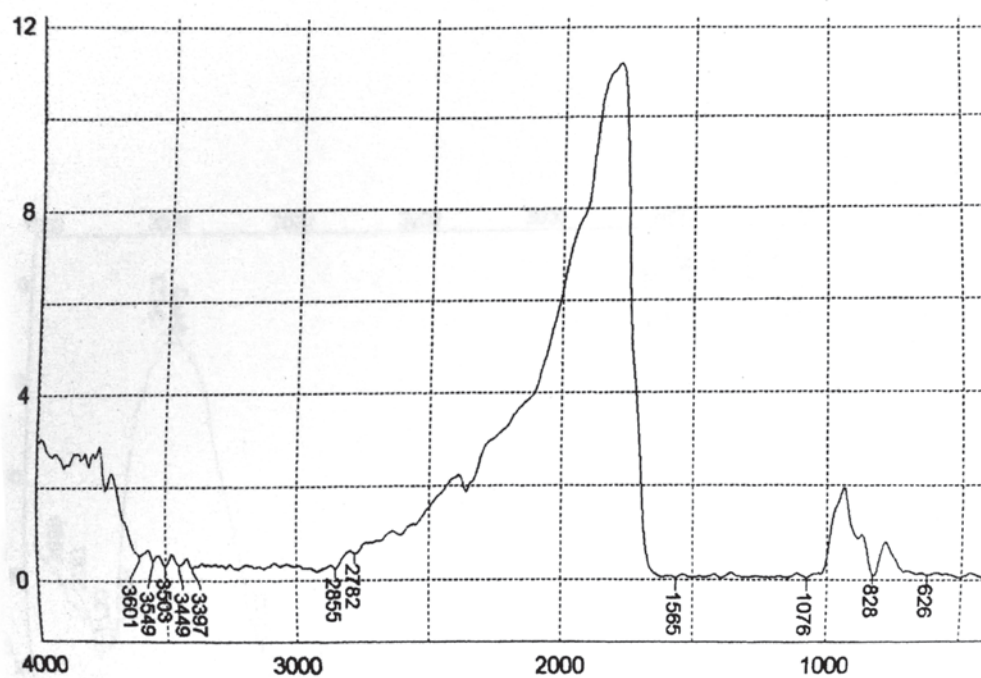
DYE-2



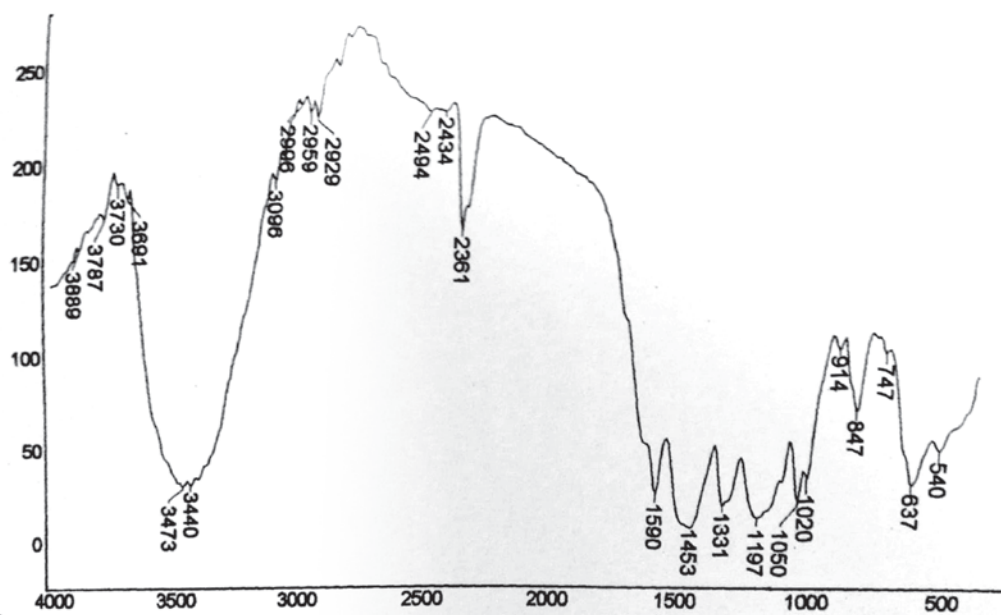
DYE-3



DYE-4



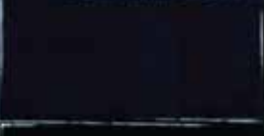
DYE-5



COLOUR CARD 1 LEATHER

NAME OF THE DYE	3% SHADE	6% SHADE
Dye 1		
Dye 2		
Dye 3		
Dye 4		
Dye 5		

COLOUR CARD 2 COTTON

NAME OF THE DYE	0.5% SHADE	1% SHADE	2% SHADE
Dye 1			
Dye 2			
Dye 3			
Dye 4			
Dye 5			