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# Synthesis and Application of Mordent and Disperse Azo Dyes Based on 2-Amino-6-Nitro-1,3- Benzothiazole

**Ashok G. Awale**
Department of Chemistry, Vinayak Ganesh Vaze College Mithaghar Road, Mulund East, Mumbai - 400081, India
ashok_awale@rediffmail.com

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## Abstract

*A diazotized solution of 2-amino-6-nitro-1,3-benzothiazole was added to the cold solution of phenols or aromatic amines to obtain azo dyes. The synthesized compounds were characterized by $^{1}$H-NMR, FT-IR, UV-Vis and LC-MS spectroscopy. Dyeing assessment of synthesized compounds was done on cotton fabric. Cotton mordant fibers showed a better hue on dyeing. Compounds were tested against representatives of gram-positive, gram- negative bacteria and fungi by agar diffusion method. The results revealed that the compounds show a broad spectrum of activity against the tested microorganisms.*

**Keywords:** Heterocycles, Benzothiazole, Aromatic amines, Diazo compounds, Biological activity.

## Introduction

Mono azo dyes are very recognizable as disperse and mordant dyes. They are consisting of major benzothiazole synthetic colorants used in the industry[1]. Azo dyes comprise approx. 65-75% of all dyes used in textile manufacture and food[2]. The different colors of azo dyes are because of extended conjugation through aromatic ring and extra stability of azo group[3]. The raw materials used in the synthesis are economical and readily available which lead to the significant production of this dyes[4-8]. Azo dyes posses better fastning properties, and are stable in the entire pH range of foods[9].

Azo dyes like azorubin and sunset yellow are widely used in the food stuffs because of low toxicity, no hyperactivity result, and less allergic property[9,10]. Azo dyes are also used in lasers, nonlinear optical systems[11], reprography[12], dye sensitized solar cells[13] and metallochromic indicators[14].

Azo dyes of benzothiazole are usually used in production of red azo dye as a result of their superior fastness properties[15-18] and exceptional dyeing properties[19-24].

A non-specific enzyme like ado - reductase originate in various microorganisms (in intestinal bacteria) and in all tested mammals can reduce and cleave azo group in to two parts[25-30], therefore we thought to find out the biological activity of prepared compounds.

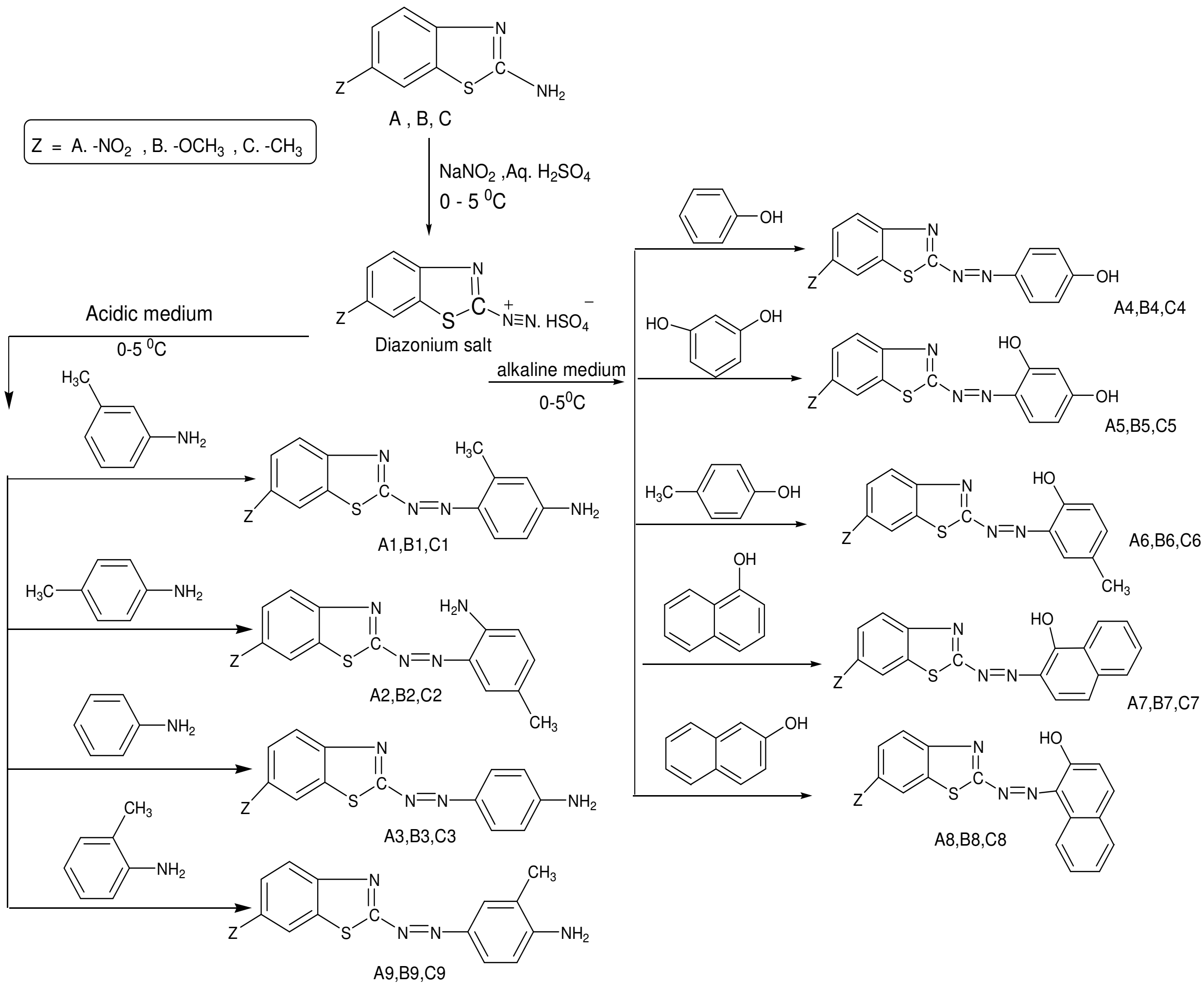
Literature survey showed that the disperse dyes of thiazoles and other hererocyclic compounds have lesser light fastness and other fastness properties, and different shades on various fabrics. It also reveals that many azo dyes are banned due to their harmful effects. The disperse dyes of 2- amino-6-nitro-1,3-benzothiazole, 2- amino-6-methoxy-1,3-benzothiazole, 2-amino-4-methyl-1,3- benzothiazole are not banned and can be produced in good yield using a simple process. Therefore it was very interesting to synthesize dyes of 2- amino-6-nitro-1,3-benzothiazole , 2- amino-6-methoxy-1,3- benzothiazole, 2-amino-4-methyl-1,3- benzothiazole and study their dyeing properties on different fabrics. In the present research we report the synthesis of azo dyes, dyeing properties, structural properties and their biological activity. To confer the different electronic environment to the molecules, a substitution pattern was properly selected.

## Materials and Methods

**Reagents, instrumentation, and measurements:** $^{1}$H NMR spectra was recorded on a Bruker AC 300 (300 MHz) in $CDCl_3$ or DMSO-$d_6$ as solvent, and TMS as an internal standard. Chemical shifts are expressed as $\delta$ ppm. IR spectra were recorded for KBr disc on a FT-IR BRUKER ALPHA-200455. LC-MS spectra were obtaind on Finnigan Incos 500 (70 ev). Melting points were measured on a Gallenklamp electrothermal melting point apparatus.

The progress of reaction was monitored by thin layer chromatography with F254 silica gel pre-coated sheets (MERCK) using toluene - ethyl acetate solvent system. The dye bath percentage exhaustion and fixation of dyed cotton fabric was determined by reported method[30]. The rubbing fastness was analyzed by Crock Meter (Atlas) AATCC-1961.

The fastness to light, sublimation and perspiration of dye pattern was analysed according to British standard: 100-1978, and wash fastness test according to Indian standard: IS: 765-1979.




**Scheme-1**
**Synthesis of Azo Dyes from 2- amino-6-nitro-1,3- benzothiazole**

***General procedure for the synthesis of 2-diazo(4'-amino-2'-methyl phenyl)-6-nitro- 1,3-benzothiazole (A1, A2, A3, A9, B1, B2, B3, B9, C1, C2, C3, C9):*** A solution of $NaNO_2$ (0.258g, 375mmol in 5mL water) was added drop wise to a solution of compound A/B/C (0.5g, 25 mmol in 15mL of 50% $H_2SO_4$) at 0-5$^0$C. The reaction mixture was maintained at 0-5$^0$C for 30 minutes. The resulting solution was added to a cold solution of m-toluidine/ p-toluidine/ aniline and o-toluidine respectively (0.267g, 25 mmol in 5mL 30% $H_2SO_4$) below 5$^0$C. The reaction mixture was stirred for 3 hrs. at 0-5$^0$C, and then for one hour at RT. The reaction mixture was treated with sodium acetate to adjust pH 7-7.5. Crude product was filtered, washed with water, and recrystallized from ethanol.

***General procedure for the synthesis of 2-diazo(4'-hydroxy phenyl)-6-nitro-1,3-benzothiazole (A4- A8, B4- B8, C4- C8):*** To a cold solution of compound A/B/C (0.5 g, 25 mmol in 15mL of 50% $H_2SO_4$) added drop wise a solution of $NaNO_2$ (0.258g, 375mmol in 5mL in water) at 0-5$^0$C. A reaction mixture was stirred for 30 minutes at 0-5$^0$C. The resulting solution was added a cold solution of phenol/resorcinol/p-cresol/1-naphthol and 2-naphthol respectively (0.258g, 275mmol in 15 mL dil. NaOH) below 5$^0$C in alkaline medium. Cold water was added to a reaction mixture and then stirred for 3 hrs. at 10$^0$C. The pH of reaction mixture was adjusted to 7-7.5. Crude product was filtered, washed with water, and recrystallized from ethanol from acetone-ethanol mixture.

***Dyeing Properties of Dyes on Cotton Fabric:*** **General procedure for dyeing of cotton with dyes (A1-C9):** The dyes were dissolved in acetone and diluted the solution with water in ratio 1:2. A cotton fabric was added to the dye bath and then heated at constant temperature 80$^0$C for 60 min. A dye bath was cooled to room temperature; fabric was washed thoroughly under tap water. The fabric was cut in two equal parts; one part of it was placed in soap solution (auxipon.NP 1.5 g/L) and heated for 20 min at 80$^0$C. The solution was cooled to room temperature; fabric was washed thoroughly with water and air dried. The UV - Vis absorption spectra of dyes were recorded in methanol. The absorption maxima ($\lambda$ max) of all dyes was found in range of 484 - 530.50 nm as shown in Table-2.

***In vitro* antimicrobial activities of azo dyes:** The synthesized dyes were evaluated for their in vitro antibacterial activity against *Staphylococcus aureus* NCIM 2079, *Basillus subtilis* NCIM 2010 as example of Gram-positive bacteria and *Escherchia coli* NCIM 2572, *Pseudomonas aeruginosa* NCIM 2053, *Salmonella typhi* NCIM 2501as example of Gram-negative bacteria. Amicacin and Gentamycin were used as standard antibacterial reference drugs. The antifungal acivity of azo dyes was tested againt *Candida albicans* NCIM 3741, *Aspergillus fumigatus* NCIM 883, *Penicillium chrysogenum* NCIM 2501 organisms using cycloheximide as reference drug. The MIC (µg/mL) and inhibition zone diameters values are recorded in Table-4.

## Results and Discussion

***2-diazo(4'-amino-2'-methyl phenyl)-6-nitro-1,3-benzothiazole (A1):*** Brown color powder, Mass-$M^+$, 313. UV-Vis λmax 530.5 nm $^1$H NMR (300MHz,$CDCl_3$, δppm): 2.1 (s, 3H, Ar'-$CH_3$), 2.6 (s, 2H, Ar'-$NH_2$) 6.5-7.2 (m,3H), 7.4-8.7 (m,4H).

***2-Diazo(2'-amino-5'-methyl phenyl)- 6-nitro-1,3-benzothiazole. (A2):*** Brown colour powder; Mass - $M^+$313, UV-Vis λmax. 445.50 nm; NMR,(300MHz, $CDCl_3$) 1.5 (s 3H,-$CH_3$), 2.2 (s 2H,-$NH_2$), 7.0-7.2 (m,3H,Ar-H), 7.0-7.2 (m,3H).

***2-Diazo(4'-amino phenyl)- 6-nitro-1,3-benzothiazole (A3):*** Dark red colour powder; Mass - $M^+$ 300.17, 259.2, 189.14 , UV-Vis λmax513.10 nm; $^1$HNMR,(300MHz, $CDCl_3$) 2.1 (s 2H,-$NH_2$) 7.2-7.5 (m,3H,Ar-H), 8.2-8.5 (m,4H,Ar'-H),

***2-Diazo(4'-hydroxy phenyl)- 6-nitro-1,3-benzothiazole (A4) (Figure: 1,2,3, and 4):*** Dark brown solid powder; Mass - $M^+$345(2 $Na^+$ salt) 289.14, 234.19. UV-Vis λ max 549.50 nm $^1$H NMR, (300MHz, $CDCl_3$) 10.6 (s,1H,-OH), 7.0-7.2 (m, 7H, Ar'-H)

***2-Diazo(2',4'-dihydroxy phenyl)-6-nitro-1,3-benzothiazole (A5):*** Brown solid powder; Mass - $M^+$ 316, 301.2, 234.25, 206.2; UV-Vis λ max 521.50 nm $^1$H NMR(300MHz, $CDCl_3$), 10.8 (s , 1H, -OH), 7.5- 8.5(m,6H, Ar-H).

***2-Diazo(2'-hydroxy-5'-methylphenyl)- 6-nitro-1,3-benzothiazole (A6) :*** Dark brown solid; Mass [M/Z (rel.Int )] , $M^+$314, 288.1, 266.1, 236.1; UV-Vis λ max453.10 nm; $^1$H NMR, (300MHz) 2.4 (s 3H,-$CH_3$) 11.7 (s ,1H,-OH) 6.7-7.8 (m,6H,Ar-H)

***2-Diazo(1'-hydroxy naphthyl)-6-nitro-1,3-benzothiazole (A7) :*** Violet colour solid; Mass - $M^+$350, UV-Vis λ max584.50 nm, $^1$H NMR,(300MHz, $CDCl_3$) 12.5( s ,1H,-OH) 7.2-7.5( m,3H,Ar-H), 8.0-8.3(m,6H,Ar'-H).

***2-Diazo(2'-hydroxynaphthyl)-6-nitro-1,3-benzothiazole (A8):*** Dark brown colour solid; Mass -$M^+$350, UV-Vis λmax 473.50 nm, 1H NMR,(300MHz, CDCl3) 11.2( s ,1H,-OH) 6.6-7.4 ( m,3H,Ar-H), 8.1-8.5(m,6H,Ar'-H).

***2-Diazo(4'-amino-3'-methyl phenyl)-6-nitro-1,3-benzothiazole (A9):*** Brown colour powder; Mass - $M^+$339($Na^+$), 301.1, 234.1; UV-Vis λmax 523.50 nm;$^1$HNMR,(300MHz, $CDCl_3$) 1.5( s 3H, -$CH_3$), 2.2( s ,2H, -$NH_2$), 7.0-7.2( m,6H,Ar-H)

***2-Diazo(4'-amino-2'-methyl phenyl)-6-methoxy-1,3-benzothiazole (B1):*** Brown powder; Mass- $M^+$ 321.1($Na^+$), 299.1,151.1; UV-Vis λmax (nm). 505.50 $^1$H NMR, (300MHz,$CDCl_3$): 2.3(s,3H,-$CH_3$), 3.8 (s,3H,- $OCH_3$), 2.9(s,2H,-$NH_2$), 6.5-7.8 (m,6H,Ar-H)

***2-Diazo(2'-amino-5'-methyl phenyl)- 6- methoxy -1,3-benzothiazole (B2):*** Dark brown color solid: Mass - $M^+$298, UV-Vis λmax 386.00 nm, $^1$H NMR,(300MHz, $CDCl_3$) 2.3( s ,3H,-$CH_3$) , 3.8(s,3H,-$OCH_3$), 3.7( s,2H,-$NH_2$), 7.0-7.6( m,6H,Ar-C-H)

***2-Diazo(4'-amino phenyl)-6-methoxy-1,3-benzothiazole (B3):*** Dark brown colour powder; Mass - $M^+$ 307($Na^+$), 233.1, 179.0; UV-Vis λmax 487.00 nm ; $^1$H NMR,(300MHz, $CDCl_3$) 3.8(s,3H,-$OCH_3$), 2.5( s,2H,-$NH_2$), 6.5-7.9( m,7H,Ar-H)

***2-Diazo(4'-hydroxyphenyl)- 6- methoxy -1,3-benzothiazole (B4):*** Dark brown solid powder; Mass- $M^+$ 285; UV-Vis λ max 507.0 nm; $^1$H NMR,(300MHz, $CDCl_3$) 10.8( s ,1H,-OH), 3.8(s,3H,-$OCH_3$), 7.0-7.1 (m,7H,Ar-H)

***2-Diazo(2',4'-dihydroxy phenyl)- 6- methoxy -1,3-benzothiazole (B5):*** Brown solid powder; Mass -$M^+$ 302.0, 181.0, 101.0; UV-Vis λ max 478.0 nm ; $^1$H NMR (300MHz, $CDCl_3$), 11.0( s ,1H,-OH), 3.8 (s,3H,-OCH3), 6.4-7.9( m,6H,Ar-H)

***2-Diazo(2'-hydroxy-5'-methylphenyl)-6-methoxy-1,3-benzothiazole(B6):*** Dark brown solid; Mass- $M^+$322.1($Na^+$), 235.2, 179; UV-Vis λ max 436.50 nm; $^1$H NMR, (300MHz, $CDCl_3$); 2.3(s, 3H,-$CH_3$), 10.6 (s,1H,-OH),3.8(s,3H,-$OCH_3$), 6.9-7.2(m,6H,Ar-H)

***2-Diazo(1'-hydroxy naphthyl)-6- methoxy -1,3-benzothiazole (B7):*** Violet colour solid; Mass - $M^+$335, UV-Vis λ max 515.0 nm; $^1$H NMR,(300MHz,$CDCl_3$) 11.1( s ,1H,-OH), 3.8(s,3H,-$OCH_3$), 6.8-7.6( m,9H, Ar-H)

***2-Diazo(2'-hydroxynaphthyl)-6- methoxy -1,3-benzothiazole (B8):*** Dark brown solid; Mass-$M^+$358.1($Na^+$), 301.2, 242.3; UV-Vis λmax 507.0 nm ; $^1$H NMR,(300MHz, $CDCl_3$); 10.6 (s,1H,-OH), 3.8 (s,3H,-$OCH_3$), 7.0-8.4 (m,9H,Ar-H)

***2-Diazo(4'-amino-3'-methyl phenyl) - 6 - methoxy-1,3-benzothiazole (B9):*** Brown solid; Mass- $M^+$298, UV-Vis λmax 494.0 nm; $^1$H NMR, (300MHz, $CDCl_3$): 2.1 (s, 3H,-$CH_3$), 3.8(s,3H,-$OCH_3$), 2.5 (s,2H,-$NH_2$), 6.7-7.9( m,6H,Ar-H)

***2-Diazo(4'-amino-2'-methyl phenyl)-6-methyl-1,3-benzothiazole (C1):*** Brown colour powder; Mass -$M^+$,283.3, 267.2; UV-Vis λmax 505 nm; [1]H NMR, (300MHz, $CDCl_3$); 1.5 (s,6H,-$CH_3$), .2(s,2H,-$NH_2$) 7.2-7.4 (m,6H,Ar-H)

***2-Diazo(2'-amino-5'-methyl phenyl)- 6- methyl -1,3-benzothiazole (C2):*** Dark brown solid; Mass-$M^+$282, UV-Vis λmax(nm). 385.0 NMR,(300MHz, CDCl3); 2.2 (s 6H,-$CH_3$), 2.9 (s 2H, -$NH_2$), 7.0-7.3( m,6H,ArC-H)

***2-Diazo(4'-amino phenyl)- 6- methyl-1,3-benzothiazole (C3):*** Dark red solid; Mass- $M^+$269.2, 206.3, UV-Vis λmax 357.0 nm; [1]HNMR, (300MHz, $CDCl_3$) 3.0 (s 2H,-$NH_2$), 2.2 (s 3H,-$CH_3$), 6.8-7.7 (m,7H,Ar-H)

***2-Diazo(4'-hydroxy phenyl)- 6- methyl-1,3-benzothiazole (C4):*** Dark brown solid; Mass-$M^+$270.2, 206.3, UV-Vis λ max 405.0 nm; [1]H NMR,(300MHz, $CDCl_3$) 11.2 (s, 1H,-OH), 2.8 (s 3H,-$CH_3$), 6.9-7.3( m,7H,Ar-H).

***2-Diazo(2',4'-dihydroxy phenyl)-6-methyl-1,3-benzothiazole (C5):*** Brown solid; Mass-$M^+$286.2, 245.0, 216.4, UV-Vis. λ max 452.0 nm; [1]H NMR(300MHz, $CDCl_3$); 10.4( s,1H,-OH), 2.4( s 3H, -$CH_3$), 7.2-8.4( m, 6H,Ar-H).

***2-Diazo(2'-hydroxy-5'-methylphenyl)- 6- methyl -1,3-benzothiazole (C6):*** Dark brown solid; Mass- $M^+$284.2, 251.2, 206.3, UV-Vis λ max 359.50 nm; [1]H NMR, (300MHz, $CDCl_3$) 2.5 (s,3H,-$CH_3$), 2.8 (s,3H,-$CH_3$), 11.5 (s,1H,-OH), 7.2-8.3 (m,6H,Ar-H).

***2-Diazo(1'-hydroxynaphthyl)- 6- methyl -1,3-benzothiazole (C7):*** Violet colour solid; Mass-$M^{+3}$ 320.2, 251.2, 210.2, UV-Vis λ max 578.0 nm; [1]H NMR, (300MHz, $CDCl_3$); 10.0 (s, 1H,-OH), 2.6( s 3H,-$CH_3$), 6.4-8.3( m,9H,Ar-H).

***2-Diazo(2'-hydroxynaphthyl)-6- methyl -1,3-benzothiazole (C8):*** Dark brown solid; Mass-$M^+$319, UV-Vis λmax 493.0 nm; [1]H NMR,(300MHz, $CDCl_3$); 9.0 (s, 1H,-OH), 2.6 (s 3H,-$CH_3$), 6.8-7.5 (m,9H, Ar-H).

***2-Diazo(4'-amino-3'-methyl phenyl)-6- methyl -1,3-benzothiazole (C9):*** Brown colour powder; Mass-$M^+$282, UV-Vis λmax 484.50 nm; [1]H NMR,(300MHz, $CDCl_3$) 2.1 (s 3H,-$CH_3$), 2.3 (s 3H,-$CH_3$), 2.8 (s ,2H,-$NH_2$) ,6.7-8.0 (m,6H,Ar-H).

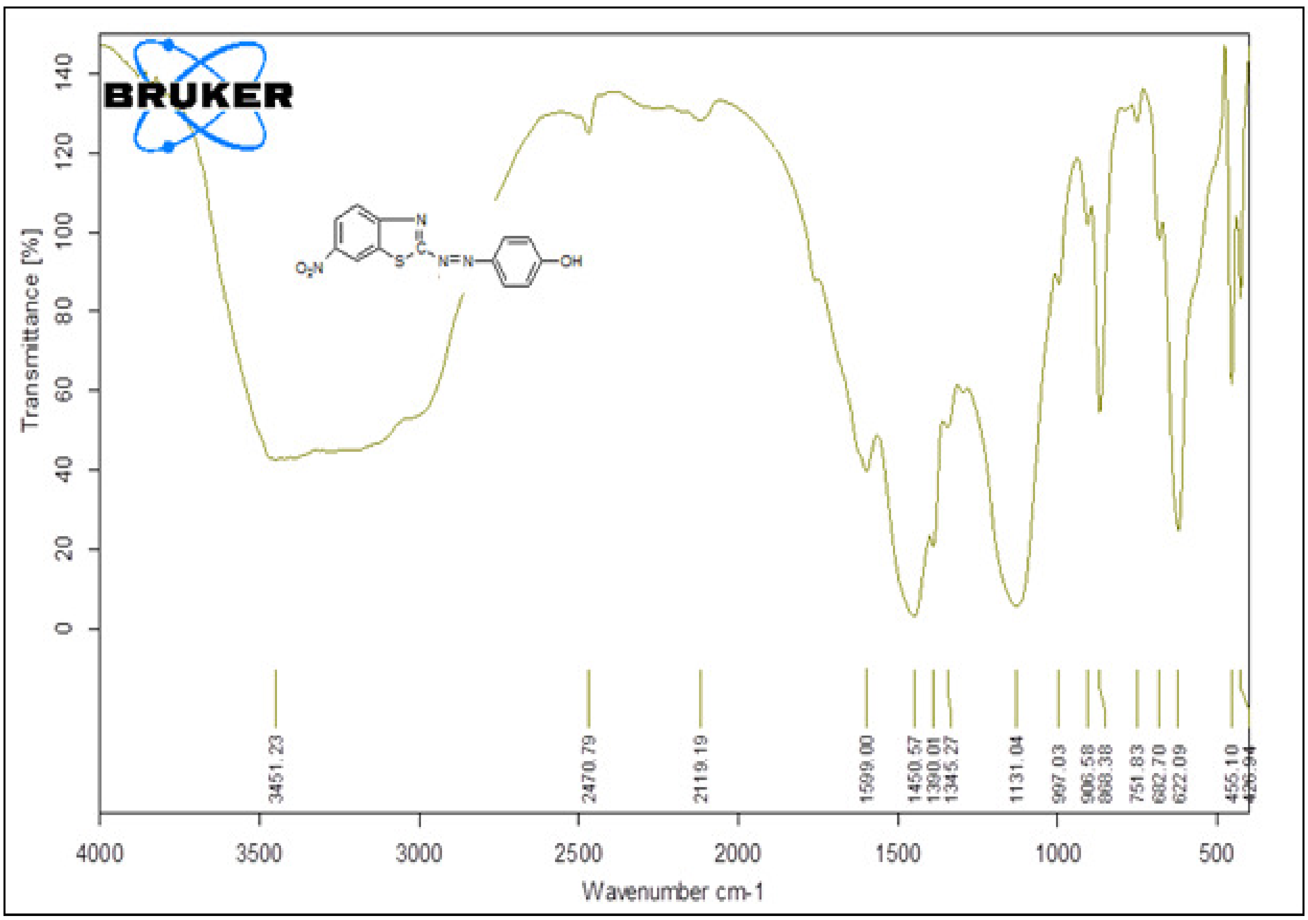



**Figure-1**
**FT-IR spectrum of 2-Diazo (4'-hydroxy phenyl)- 6-nitro-1,3-benzothiazole (A4)**

**Table-1**
**Physical data of synthesized dyes** ***(Spectrum as Figure: 1,2,3, and 4)***

| Dye | Mol. Formula | Mol. wt. | % yield | M.P. $^{0}C$ | IR ($cm^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | -N=N | -C=N Thiazole | ArC-H | Substituent |
| A1 | $C_{14}H_{11}N_5SO_2$ | 313 | 73.1 | 250 -252 | 1606 | 1573 | 3059 | 3464 -N-H, 1336-$NO_2$ |
| A2 | $C_{14}H_{11}N_5SO_2$ | 313 | 71.9 | 130 -132 | 1637 | 1580 | 3055 | 3402 -N-H, 1352-$NO_2$ |
| A3 | $C_{13}H_9N_5SO_2$ | 299 | 75.0 | 210 -212 | 1637 | 1565 | 3120 | 3403 -N-H, 1331-$NO_2$ |
| A4 | $C_{13}H_8N_4SO_3$ | 300 | 70.9 | 250 -252 | 1599 | 1495 | 2960 | 3451-OH, 1345-$NO_2$ |
| A5 | $C_{13}H_8N_4SO_4$ | 316 | 75.0 | 205 -207 | 1603 | 1511 | 3187 | 3415-OH, 1333-$NO_2$ |
| A6 | $C_{14}H_{10}N_4SO_3$ | 314 | 72.0 | 235 -237 | 1622 | 1517 | 3101 | 3404-OH, 1337-$NO_2$ |
| A7 | $C_{17}H_{10}N_4SO_3$ | 350 | 73.6 | 240 -242 | 1537 | 1520 | 3103 | 3443-OH, 1334-$NO_2$ |
| A8 | $C_{17}H_{10}N_4SO_3$ | 350 | 75.0 | 235 -237 | 1602 | 1532 | 3099 | 3457-OH, 1329-$NO_2$ |
| A9 | $C_{14}H_{11}N_5SO_2$ | 313 | 72.9 | 180 -182 | 1552 | 1603 | 3162 | 3449-OH, 1323-$NO_2$ |
| B1 | $C_{15}H_{14}N_4SO$ | 298 | 71.7 | 150 -152 | 1606 | 1549 | 3005 | 3451-NH,1186-$OCH_3$ |
| B2 | $C_{15}H_{14}N_4SO$ | 298 | 79.4 | 250 -252 | 1608 | 1506 | 3020 | 3445-NH, 1264-$OCH_3$ |
| B3 | $C_{14}H_{12}N_4SO$ | 284 | 72.2 | 200 -202 | 1601 | 1489 | 3030 | 3383-NH, 1223-$OCH_3$ |
| B4 | $C_{14}H_{11}N_3SO_2$ | 285 | 72.4 | 310 -312 | 1603 | 1497 | 3035 | 3406-OH, 1387-$OCH_3$ |
| B5 | $C_{14}H_{11}N_3SO_3$ | 301 | 69.7 | 290 -292 | 1631 | 1598 | 3129 | 3500-OH, 1245-$OCH_3$ |
| B6 | $C_{15}H_{13}N_3SO_2$ | 299 | 79.6 | 298 -300 | 1603 | 1489 | 3013 | 3389-OH, 1270-$OCH_3$ |
| B7 | $C_{18}H_{13}N_3SO_2$ | 335 | 79.5 | 230 -232 | 1598 | 1487 | 3004 | 3438-OH, 1272-$OCH_3$ |
| B8 | $C_{18}H_{13}N_3SO_2$ | 335 | 81.0 | 205 -207 | 1604 | 1469 | 3125 | 3520-OH, 1264-$OCH_3$ |
| B9 | $C_{15}H_{14}N_4SO$ | 298 | 76.2 | 250 -252 | 1601 | 1482 | 3128 | 3424-NH, 1252-$OCH_3$ |
| C1 | $C_{15}H_{14}N_4S$ | 282 | 79.9 | 320 -222 | 1641 | 1537 | 3128 | 3429-NH, 3008-$CH_3$ |
| C2 | $C_{15}H_{14}N_4S$ | 282 | 73.2 | 210 -212 | 1627 | 1460 | 3162 | 3418-NH, 2976-$CH_3$ |
| C3 | $C_{14}H_{12}N_4S$ | 268 | 79.0 | 340 -342 | 1628 | 1550 | 3117 | 3421-NH, 2975-$CH_3$ |
| C4 | $C_{14}H_{11}N_3SO$ | 269 | 76.8 | 220 -222 | 1623 | 1582 | 3046 | 3464-OH, 2969-$CH_3$ |
| C5 | $C_{14}H_{11}N_3SO_2$ | 285 | 74.9 | 328 -330 | 1630 | 1533 | 3047 | 3445-OH, 2984-$CH_3$ |
| C6 | $C_{15}H_{13}N_3SO$ | 283 | 73.1 | 240 -242 | 1632 | 1528 | 3063 | 3425-OH, 2971-$CH_3$ |
| C7 | $C_{18}H_{13}N_3SO$ | 319 | 80.2 | 260 -262 | 1629 | 1535 | 3022 | 3422-OH, 2963-$CH_3$ |
| C8 | $C_{18}H_{13}N_3SO$ | 319 | 78.2 | 310 -312 | 1627 | 1531 | 3044 | 3447-OH, 2954-$CH_3$ |
| C9 | $C_{15}H_{14}N_4S$ | 282 | 79.0 | 180 -182 | 1626 | 1426 | 3037 | 3486-NH, 2969-$CH_3$ |

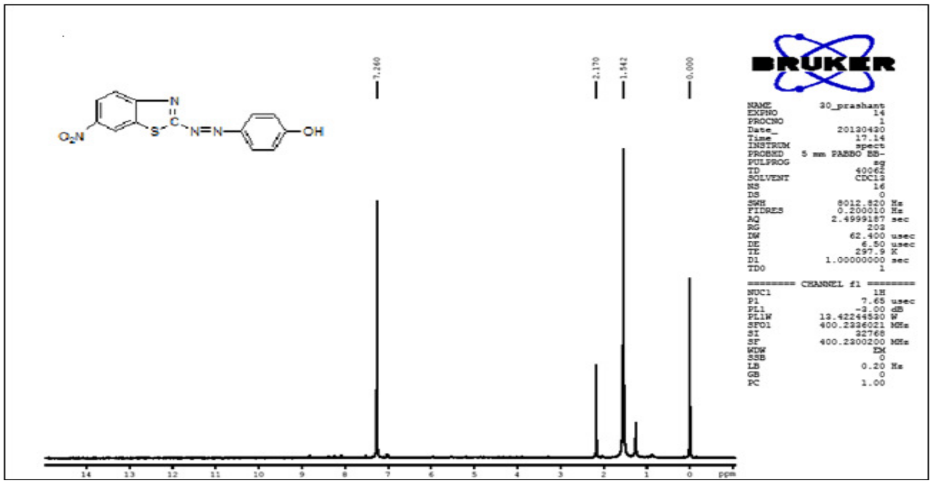



**Figure-2**
**[1]HNMR spectrum of 2-Diazo (4'-hydroxy phenyl)- 6-nitro-1,3-benzothiazole (A4)**

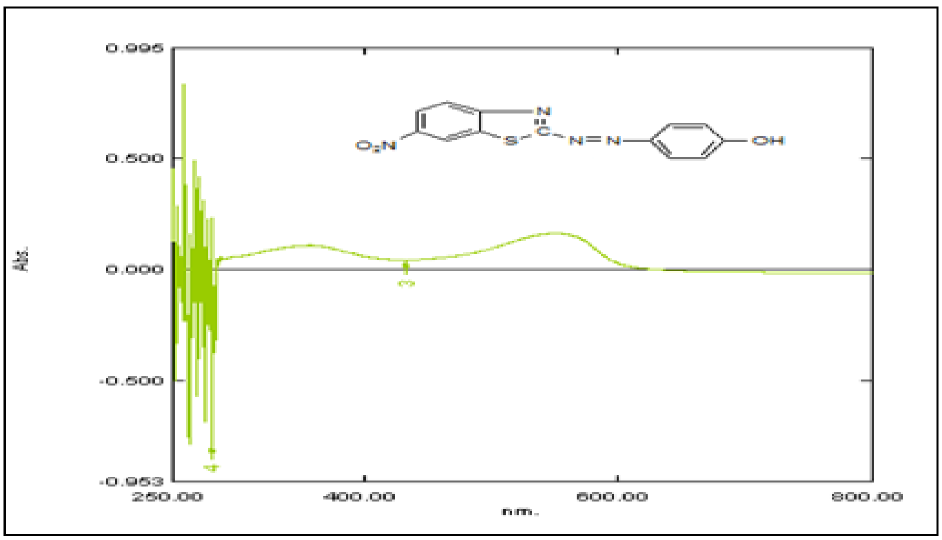



**Figure-3**
**UV-Visible spectrum of 2-Diazo(4'-hydroxy phenyl)- 6-nitro-1,3-benzothiazole (A4)**

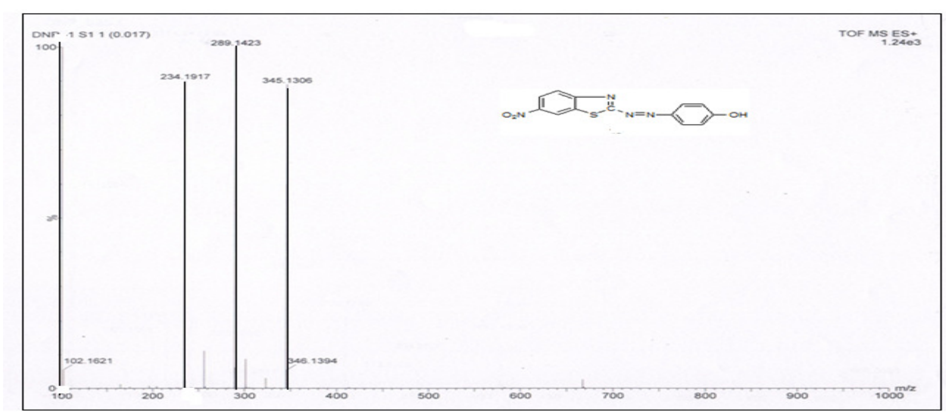



**Figure-4**
**Mass spectrum of 2-Diazo (4'-hydroxy phenyl)- 6-nitro-1,3-benzothiazole (A4)**

**Table-2**
**Absorption maxima ($\lambda_{max}$), exhaustion (E) and fixation (F) on cotton fabric**

| Dye Compounds | ( $\lambda_{max}$ ) nm, methanol | Rf (cm) | Dyeing on cotton % | |
|---|---|---|---|---|
| | | | Exhaustion E | Fixation F |
| A1 | 530.50 | 0.5 | 72 | 91 |
| A2 | 445.50 | 0.4 | 72 | 92 |
| A3 | 513.00 | 0.5 | 73 | 89 |
| A4 | 549.50 | 0.6 | 76 | 93 |
| A5 | 521.50 | 0.6 | 70 | 92 |
| A6 | 453.00 | 0.4 | 71 | 90 |
| A7 | 584.50 | 0.4 | 82 | 92 |
| A8 | 473.50 | 0.5 | 78 | 93 |
| A9 | 523.50 | 0.4 | 74 | 94 |
| B1 | 505.40 | 0.5 | 75 | 95 |
| B2 | 386.00 | 0.6 | 72 | 94 |
| B3 | 487.00 | 0.5 | 77 | 92 |
| B4 | 507.00 | 0.5 | 80 | 96 |
| B5 | 478.00 | 0.6 | 82 | 93 |
| B6 | 436.50 | 0.5 | 80 | 92 |
| B7 | 515.00 | 0.4 | 76 | 94 |
| B8 | 507.00 | 0.5 | 72 | 90 |
| B9 | 494.00 | 0.6 | 76 | 93 |
| C1 | 505.00 | 0.5 | 76 | 85 |
| C2 | 385.00 | 0.6 | 81 | 84 |
| C3 | 357.00 | 0.4 | 83 | 87 |
| C4 | 405.00 | 0.5 | 80 | 83 |
| C5 | 452.00 | 0.4 | 71 | 80 |
| C6 | 359.50 | 0.4 | 70 | 86 |
| C7 | 578.00 | 0.4 | 72 | 88 |
| C8 | 493.00 | 0.6 | 70 | 80 |
| C9 | 484.00 | 0.5 | 73 | 87 |

**Table-3**
**Dyeing and various fastness properties of dyes on a cotton fabric**

| Dye | Color shades on cotton | Light fastness | Washing fastness | Sublimation fastness | Perspiration fastness | | Rubbing fastness | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Acid | Alkali | Dry | Wet |
| A1 | Orange | 5 | 4 | 5 | 5 | 5 | 5 | 3.5 |
| A2 | Orange | 5 | 4 | 5 | 4 | 5 | 5 | 4.0 |
| A3 | Pink | 5 | 4 | 5 | 4 | 4 | 5 | 4.5 |
| A4 | Violet | 5 | 5 | 5 | 5 | 5 | 5 | 4.0 |
| A5 | Violet | 5 | 5 | 4 | 4 | 3 | 4 | 3.0 |
| A6 | Gray | 5 | 5 | 5 | 4 | 5 | 5 | 3.0 |
| A7 | Blue | 5 | 4 | 5 | 4 | 4 | 4 | 3.0 |
| A8 | Orange | 5 | 5 | 5 | 5 | 4 | 5 | 3.5 |
| A9 | Brown | 5 | 4 | 5 | 4 | 4 | 4 | 4.0 |
| B1 | Orange | 5 | 4 | 5 | 4 | 4 | 5 | 4.5 |
| B2 | Yellow | 5 | 4 | 5 | 4 | 4 | 5 | 4.5 |
| B3 | Red | 5 | 4 | 5 | 4 | 5 | 5 | 4.0 |
| B4 | Brown | 5 | 5 | 5 | 5 | 5 | 5 | 4.5 |
| B5 | Brown | 5 | 5 | 5 | 5 | 5 | 5 | 3.5 |
| B6 | Saffron | 5 | 5 | 5 | 5 | 4 | 5 | 3.0 |
| B7 | Blue | 5 | 5 | 5 | 4 | 4 | 5 | 3.0 |
| B8 | Pink | 5 | 4 | 5 | 5 | 4 | 5 | 3.0 |
| B9 | Orange | 5 | 5 | 5 | 4 | 4 | 4 | 4.5 |
| C1 | Orange | 5 | 4 | 5 | 4 | 3 | 4 | 4.0 |
| C2 | Yellow | 5 | 4 | 5 | 4 | 3 | 4 | 4.0 |
| C3 | Saffron | 5 | 4 | 5 | 4 | 4 | 4 | 4.0 |
| C4 | Violet | 5 | 5 | 5 | 4 | 5 | 4 | 4.0 |
| C5 | Yellow | 5 | 5 | 5 | 4 | 4 | 4 | 3.0 |
| C6 | Violet | 5 | 4 | 5 | 4 | 4 | 4 | 3.5 |
| C7 | Gray | 5 | 4 | 5 | 4 | 3 | 3 | 3.0 |
| C8 | Pink | 5 | 4 | 5 | 4 | 3 | 3 | 3.0 |
| C9 | Red | 5 | 4 | 5 | 3 | 3 | 3 | 4.0 |

**Table-4**
***In vitro* antimicrobial activities of azo dyes**

| **Compound** | **Bacteria** | | | | | **Fungi** | |
|---|---|---|---|---|---|---|---|
| | **Gram +** | | **Gram –** | | | | |
| | ***B .subtilis*** | ***S. aureus*** | ***S.typhi*** | ***E. coli*** | ***P.aeruginosa*** | ***C.albicans*** | ***As. fumigates*** |
| A1 | 12 | 14 | 10 | 13 | 15 | 12 | 10 |
| A2 | 14 | 21 | 12 | 13 | 10 | 10 | 10 |
| A3 | 13 | 08 | 10 | 12 | 12 | 13 | 15 |
| A4 | 15 | 05 | 07 | 12 | 11 | 11 | 12 |
| A5 | 13 | 20 | 11 | 14 | 08 | 10 | 13 |
| A6 | 12 | 11 | 10 | 11 | 10 | 11 | 06 |
| A7 | 15 | 10 | 11 | 11 | 10 | 11 | 11 |
| A8 | 11 | 09 | 12 | 16 | 12 | 12 | 12 |
| A9 | 12 | 13 | 13 | 10 | 10 | 11 | 14 |
| B1 | 19 | 20 | 10 | 14 | 10 | 13 | 14 |
| B2 | 18 | 22 | 10 | 12 | 14 | 11 | 08 |
| B3 | 18 | 22 | 10 | 14 | 12 | 13 | 11 |
| B4 | 18 | 23 | 10 | 13 | 11 | 11 | 10 |
| B5 | 17 | 24 | 09 | 15 | 11 | 10 | 11 |
| B6 | 20 | 21 | 12 | 14 | 10 | 11 | 12 |
| B7 | 20 | 18 | 11 | 14 | 10 | 09 | 15 |
| B8 | 18 | 21 | 11 | 14 | 11 | 12 | 10 |
| B9 | 19 | 18 | 12 | 10 | 13 | 15 | 17 |
| C1 | 19 | 11 | 10 | 08 | 06 | 11 | 12 |
| C2 | 18 | 11 | 11 | 08 | 06 | 10 | 14 |
| C3 | 16 | 11 | 14 | 10 | 08 | 11 | 11 |
| C4 | 18 | 14 | 11 | 10 | 12 | 13 | 10 |
| C5 | 18 | 12 | 12 | 10 | 10 | 11 | 10 |
| C6 | 21 | 12 | 10 | 10 | 10 | 10 | 12 |
| C7 | 12 | 11 | 10 | 11 | 11 | 11 | 10 |
| C8 | 15 | 13 | 12 | 11 | 11 | 15 | 14 |
| C9 | 16 | 15 | 11 | 13 | 12 | 11 | 14 |
| Amicacin | 20 | 17 | 30 | 30 | 29 | NT | NT |
| Gentamycin | 34 | 33 | 22 | 22 | 22 | NT | NT |
| *Cycloheximide* | NT | NT | NT | NT | NT | 25 | 31 |

Zone of inhibition in mm. *Less active: 6–12 mm; moderately active: 13–19 mm; highly active: 20–30 mm; No inhibition or inhibition less than 5 mm; NT: not tested.

The synthesized compounds obtained were of high purity and yields above 70%. The dyes showed wide range of colors varying from orange to reddish brown shades with excellent smoothness, brightness and depth on cotton fabric. Dyeing properties are recorded in (Table-2 and 3). The variation in shades of dye fabrics can be attributed to the nature and position of substituent (auxochrome) present with respect to N=N in dye structure. It was found that N=N is an electron withdrawing group and auxochrome like $-NH_2$, $-NR_2$, -OH and electron releasing groups, when conjugated through double bonds, electrons move from auxochrome to N=N. The results revealed that the larger separation of -N=N group and auxochrome increases the resonance and intensity of color. The dyes showed an excellent fastness to light, washing, perspiration and sublimation. Rubbing fastness of dyes was found fairly well. It was observed that the dye fabric showed remarkable degree of smoothness which can be attributed to the association of cotton molecule with the dye. The results obtained also have characterized and identified dye degrading efficiency of *S.aureus*, *B subtilis E.coli*, *Ps. aeruginosa*, *S. typhi*, *C. albicans, As. fumigates*, *Penicillium chrysogenum.* The ability of the strain to tolerate, decolorize and degrade azo dyes at high concentration gives it an advantage for treatment of textile industry wastewater. The strains could decolorize most of the azo dyes by 70- 100% within 24 h under the optimum conditions of static condition, pH 7.0, temperature of $37^0$C and initial dye concentration of 500 mg/l. The result shows that the selected culture has good potential in decolourization and degradation of azo dyes under static conditions.

## Conclusion

The compounds were obtained in pure form, yields above 70% and solids with free flowing nature. The brilliant shades of colors are obtained on cotton fabric with excellent smoothness, brightness and depth on cotton fabric. The dyed fabrics showed an excellent fastness to light and good to excellent fastness to washing, perspiration and sublimation, and rubbing fastness.

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