Synthesis of New Congo Red Derivative Dyes and their Application as Hardness Reduction in Hard Water.

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Summary: Azo dyes are exceptionally important in a variety of industries for diverse technical purposes. Synthesis of new Congo Red derivatives **(6a-j)** was achieved by diazotization of Congo Red at low temperature followed by coupling with a number of different coupling partners **5a-j** in basic medium. The structures of newly synthesized dyes were confirmed using elemental and spectral data. The synthesized dyes were tested for their ion scavenging properties in hard water. Compounds **6b-d** and **6h-i** were found to be successful in decreasing the water hardness, making them valuable candidates for water treatment in boilers and cooling towers in the chemical industry.

Key words: Congo Red dye, Diazotization, Spectroscopic techniques, Water hardness.

Introduction

Azo dyes constitute 60-70% of all the synthetic dyes being used as commercial colorants. Azo compounds are continuously gaining attention in scientific research because of variety of derivatives obtained by the slight modifications of dye intermediate structures [1, 2, 3]. Excellent thermal and optical properties of azo dyes have made them a field of diverse applications such as optical recording medium, toner [4], ink-jet printing [5], and oil-soluble light fast dyes. Biocidal treatment of textile materials is being done by azo dyes of suitable structures carrying some bioactive templates which exhibit physical interactions and chemical bonding with molecules of fibrous materials [6, 7]. Medicinal importance of azo compounds is also well documented because of their use as antineoplastics [8], antidiabetics, antiseptics [9], antibacterial [10] and antitumor [11]. In a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation [12, 13], the involvement of azo dyes is known.

Applications of azo dyes are not only limited to textile materials but also to leather, aluminum sheet, ink-jet printer, paper, electro-optical devices [14]. Azo dyes are being used in different fields because of their interesting electronic properties in concern to their applications in for molecular memory storage, nonlinear optical elements and wide variety of hues ranging from blue to red of the visible region of electromagnetic radiation spectrum. Methyl orange, methyl red and Congo red are the dyes being used as acid base indicators because of their ability to act as weak acids or bases. Electronic delocalization and tautomerism are responsible for color change in these dyes on changing pH of medium. In the pharmaceutical and medicinal fields azo compounds are becoming important [15] and it has been proposed that the biological activities expressed by some reported Schiff bases [16, 17], might be due to azoimine linkage. Presence of azo linkage is one of those structural features which are responsible for antibacterial and pesticidal activities of different types of compounds. Substantial attention has given to azo dyes, to achieve antimicrobial properties in them [18].

Keeping in view the above mentioned importance of azo dyes and the congo red dye it was conceivable to develop synthesis of the congo dye derivatives in connection with their applications for removal of hardness of hard water.

Experimental

Materials and Methods

All commercial products were purchased from Sigma-Aldrich. Solvents used were of analytical grade and when necessary were purified and dried by the standard methods. Melting points were recorded in open capillary tubes using a digital Gallenkamp (SANYO) model MPD.BM 3.5 apparatus and are uncorrected. The FTIR spectra were run in the single beam Nicolet IR 100 (Fourier-Transform); and ultraviolet-visible (UV-VIS) spectra were recorded on a double beam Perkin-Elmer Lambda 900 UV-VIS-NIR spectrophotometer. The ^{1}H-NMR spectra were taken in DMSO using NMR Bruker DPX 400 spectrophotometer operating at 300 MHz. Tetramethyl silane (TMS) was used as internal standard and chemical shifts δ recorded in ppm. The pH was monitored using Portable pH Meter Model PHB4. Elemental analyses were conducted using a

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LECO-183 CHNS analyzer. Compounds were routinely checked by thin layer chromatography (TLC) on silica gel G plates using ethyl acetate: ethanol (1:1) as the solvent systems. Also the developed plates were visualized using UV lamp for the presence of spots. All crude products were isolated as solids and purified by a combination of column chromatography and recrystallization. Application of dyes for hardness removal were performed by using the standard method of volumetric titration for hardness determination using ethylenediamine tetraacetate dehydrate (EDTA), Eriochrome black T and ammonia buffer pH=10.

General Procedure for the Synthesis Congo Red Dye Derivatives **(6a-j)**

In an ice jacketed 100 ml beaker, benzidine (0.01mol) was dissolved in acidified water (15 ml, hydrochloric acid 36.5%, 2.5 ml) at room temperature. To the well stirred solution was added sodium nitrite (0.002mol) and agitated the reaction mixture for 1 hour at 0-5^{o}C. Afterward addition of sodium naphthionate (0.02 mol) was made dropwise in half hour. Stirred the reaction mixture 1h more at the same temperature and checked the completion of reaction by taking the TLC (ethyl acetate: ethanol 1:1). At completion dye was salted out from 15% NaCl solution. The dye was filtered, dried and recrystallized from ethanol.

Congo red dye 0.001mol aqueous solution was stirred well in a 100 ml beaker and diazotized at 0-5^{o}C with nitrous acid generated in situ by addition of HCl 36.5% (2ml) and sodium nitrite (0.002mol). Continuously stirring the reaction mixture for 1h at this temperature was treated with couplers **5a-j** (0.002mol) in basic medium and prepared dyes **6a-j** according to scheme-1. Physical and spectral characterization data of these dyes ia as follows:

Sodium 3,3'-((1E,1'E)-(((1E,1'E)-[1,1'-biphenyl]-4,4'-diylbis(diazene-2,1-diyl))bis(4-sulfonatonaphthalene-2,1-diyl))bis(diazene-2,1-diyl))bis(5-amino-4-hydroxynaphthalene-2,7-disulfonate) (**6a**)

Violet red, m.p> 300 ^{o}C; R_f: 0.31 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3325 (br), 1716, 1604, 1496, 1162, 1045, 818, 764 cm^{-1}; ^{1}H-NMR (DMSO 300 MHz) δ (ppm): 7.95 (d, 4H, 7Hz, Ar-H), 7.63 (d, 4H, Ar-H, 7.5 Hz), 7.49 (d, 2H, 7.3Hz, Ar-H), 7.58 (d, 2H, 7.2 Hz, Ar-H), 7.78 (t, 2H, 7Hz, Ar-H), 7.87 (t, 2H, 7Hz), 7.7 (s, 2H, Ar-H), 7.8 (s, 2H, Ar-H), 7.92 (s, 2H, Ar-H), 4.0 (br s, 4H, N-H), 6.3 (br s, 2H, O-H); Anal. Calcd. For $C_{52}H_{30}N_{10}O_{20}S_6Na_6$ C,43.21; H, 2.08; N,9.69; S, 13.30; Found: C,43.10; H,2.00; N,9.60; S, 13.35.

Sodium 5,5'-((1E,1'E)-(((1E,1'E)-[1,1'-biphenyl]-4,4'-diylbis(diazene-2,1-diyl))bis(4-sulfonatonaphthalene-2,1-diyl))bis(diazene-2,1-diyl))bis(6-hydroxynaphthalene-2-sulfonate) **(6b)**

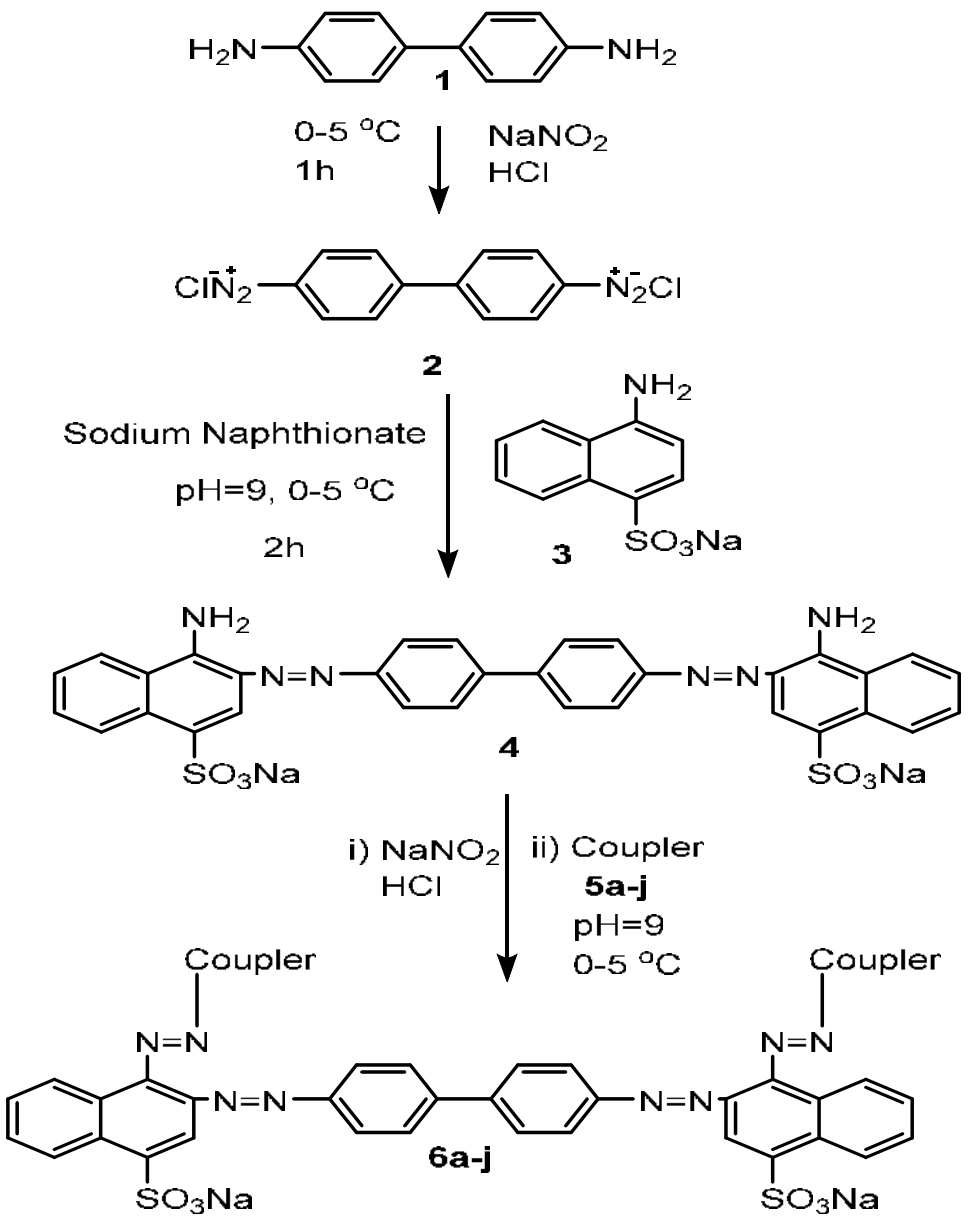
Violet red, m.p> 300 ^{o}C; R_f: 0.34 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3520, 3015, 1738,1613, 1434, 1199, 1048, 874, 820, 617 cm^{-1}. ^{1}H-NMR (DMSO 300 MHz) δ (ppm): 7.97 (d, 4H, 7Hz, Ar-H), 7.69 (d, 4H, Ar-H, 7.5 Hz), 7.45 (d, 2H, 7.3Hz, Ar-H), 7.53 (d, 2H, 7.2 Hz, Ar-H), 7.78 (t, 2H, 7Hz, Ar-H), 7.84 (t, 2H, 7Hz), 8.3 (s, 2H, Ar-H), 8.0 (d, 2H, Ar-H, 7.5Hz),7.8(d, 2H, Ar-H, 7.5Hz), 7.6 (d, 2H, Ar-H, 7.3Hz) 7.0 (d, 2H, Ar-H, 7.5Hz), 4.8 (br s, 4H), 6.7 (br s, 2H); Anal. Calcd. For $C_{52}H_{30}N_8O_{14}S_4Na_4$: C, 51.57; H, 2.48; N,9.3; S, 7.60; Found: C, 51.50; H, 2.37; N, 9.22; S, 7.65.

Sodium 4-((E)-(2-hydroxynaphthalen-1-yl)diazenyl)-3-((E)-(4'-((E)-(1-((E)-(2-hydroxynaphthalen-1-yl)diazenyl)-4-sulfonatonaphthalen-2-yl)diazenyl)-[1,1'-biphenyl]-4-yl)diazenyl)naphthalene-1-sulfonate **(6c)**

Brownish red, m.p> 300 ^{o}C; R_f: 0.41 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3510(br), 3044,1614, 1575, 1445, 1204, 1093, 884, 822, 638 cm^{-1}. ^{1}H-NMR (DMSO 300 MHz) δ (ppm): 7.89 (d, 4H, 7Hz, Ar-H), 7.65 (d, 4H, Ar-H, 7.5 Hz), 7.53 (d, 2H, 7.3Hz, Ar-H), 7.58 (d, 2H, 7.2 Hz, Ar-H), 7.79 (t, 2H, 7Hz, Ar-H), 7.83 (t, 2H, 7Hz, Ar-H), 7.6 (d, 2H, 7.3Hz, Ar-H), 7.6 (d, 2H, 7.7Hz, Ar-H), 7.45 (d, 2H, 7.7Hz, Ar-H), 7.33 (t, 2H, 7.4Hz, Ar-H), 7.2 (t, 2H, 7.5Hz, Ar-H), 7.0 (d, 2H, 7.3Hz, Ar-H), 6.3 (br s, 2H); Anal. Calcd. For $C_{52}H_{32}N_8O_8S_2Na_2$: C, 62.02; H, 3.18; N,11.13; S, 6.36; Found: C, 61.90; H, 3.13; N,11.31; S, 6.27.

Sodium 4-((E)-(6-amino-1-hydroxy-3-sulfonatonaphthalen-2-yl)diazenyl)-3-((E)-(4'-((E)-(1-((E)-(7-amino-1-hydroxy-3-sulfonatonaphthalen-2-yl)diazenyl)-4-sulfonatonaphthalen-2-yl)diazenyl)-[1,1'-biphenyl]-4-yl)diazenyl)naphthalene-1-sulfonate **(6d)**

Brownish red, m.p> 300 ^{o}C; R_f: 0.37 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3545(br), 3040, 1708, 1630, 1565, 1430, 1190, 1095, 880, 816, 635 cm^{-1}. ^{1}H-NMR (DMSO 300 MHz) δ (ppm): 7.98 (d, 4H, 7Hz, Ar-H), 7.67 (d, 4H, Ar-H, 7.5 Hz), 7.51 (d, 2H, 7.3Hz, Ar-H), 7.58 (d, 2H, 7.2 Hz, Ar-H), 7.78 (t, 2H, 7Hz, Ar-H), 7.83 (t, 2H, 7Hz Ar-H), 6.8 (s, 2H, Ar-H) 7.8 (s, 2H, Ar-H), 7.0 (d, 2H, Ar-H, 7.5Hz), 7.9 (d, 2H, Ar-H, 7.5Hz), 6.6 (br s, 2H, O-H); Anal. Calcd. For $C_{52}H_{32}N_{10}O_{14}S_4Na_4$: C,50.32; H, 2.58; N,11.29; S, 10.32; Found: C, 50.10; H, 2.53; N,11.25; S, 10.15.



Scheme-1: Synthetic route to congo red derivatives (**6a-j**).

Sodium 5,5'-((1E,1'E)-(((1E,1'E)-[1,1'-biphenyl]-4,4'-diylbis(diazene-2,1-diyl))bis(4-sulfonatonaphthalene-2,1-diyl))bis(diazene-2,1-diyl))bis(2,4-diaminobenzenesulfonate) **(6e)**

Brownish red, m.p> 300 °C; R_f: 0.38 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3325, 3080,1625, 1582, 1444, 1230, 1081, 873, 825, 643 cm^{-1}. ^{1}H-NMR (DMSO 300 MHz) δ (ppm): 7.98 (d, 4H, 7Hz, Ar-H), 7.66 (d, 4H, Ar-H, 7.5 Hz), 7.5 (d, 2H, 7.3Hz, Ar-H), 7.55 (d, 2H, 7.2 Hz, Ar-H), 7.75 (t, 2H, 7Hz, Ar-H), 7.85 (t, 2H, 7Hz Ar-H), 5.9 (s, 2H, Ar-H), 7.4 (s, 2H, Ar-H), 6.0 (s, 2H), 4.8 (br s 8H); Anal. Calcd. For $C_{44}H_{30}N_{12}O_{12}S_4Na_4$: C,46.39; H, 2.63; N,14.76; S, 11.24; Found: C,45.90; H, 2.56; N,14.85; S, 11.40.

Sodium 4-((E)-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)diazenyl)-3-((E)-(4'-((E)-(1-((E)-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)diazenyl)-4-sulfonatonaphthalen-2-yl)diazenyl)-[1,1'-biphenyl]-4-yl)diazenyl)naphthalene-1-sulfonate **(6f)**

Yellowish red, m.p> 300 °C; R_f: 0.45 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3120, 1722,

1619, 1576, 1447, 1208, 1065, 864, 817, 667 cm^{-1}. ^{1}H-NMR (DMSO 300 MHz) δ (ppm): 7.90 (d, 4H, 7Hz, Ar-H), 7.63 (d, 4H, Ar-H, 7.5 Hz), 7.53 (d, 2H, 7.3Hz, Ar-H), 7.59 (d, 2H, 7.2 Hz, Ar-H), 7.78 (t, 2H, 7Hz, Ar-H), 7.83 (t, 2H, 7Hz Ar-H), 7.24-7.46 (m, 10H, Ar-H); Anal. Calcd. For $C_{52}H_{36}N_{12}O_8S_2Na_2$: C, 58.53; H, 3.38; N,15.76; S, 6.00; Found: C, 58.40; H, 3.10; N,15.70; S, 6.3.

Sodium 4-((E)-(3-methyl-5-oxo-1-(4-sulfonatophenyl)-4,5-dihydro-1H-pyrazol-4-yl)diazenyl)-3-((E)-(4'-((E)-(1-((E)-(3-methyl-5-oxo-1-(4-sulfonatophenyl)-4,5-dihydro-1H-pyrazol-4-yl)diazenyl)-4-sulfonatonaphthalen-2-yl)diazenyl)-[1,1'-biphenyl]-4-yl)diazenyl)naphthalene-1-sulfonate **(6g)**

Yellowish red, m.p> 300 ^{o}C; R_f: 0.39 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3072 1715, 1615, 1570, 1453, 1170, 1080, 861, 811, 660 cm^{-1}.^{1}H-NMR (DMSO 300 MHz) δ (ppm): 7.934 (d, 4H, 7Hz, Ar-H), 7.60 (d, 4H, Ar-H, 7.5 Hz), 7.50 (d, 2H, 7.3Hz, Ar-H), 7.57 (d, 2H, 7.2 Hz, Ar-H), 7.73 (t, 2H, 7Hz, Ar-H), 7.84 (t, 2H, 7Hz Ar-H), 7.91-7.92 ppm (m, 8H, Ar-H); Anal. Calcd. For $C_{52}H_{34}N_{12}O_{14}S_4Na_4$: C, 49.13; H, 2.68; N,13.22; S, 10.08; Found: C, 48.90; H, 2.60; N, 12.98; S, 10.00.

Sodium 4-((E)-(2,4-dihydroxyphenyl)diazenyl)-3-((E)-(4'-((E)-(1-((E)-(2,4-dihydroxyphenyl)diazenyl)-4-sulfonatonaphthalen-2-yl)diazenyl)-[1,1'-biphenyl]-4-yl)diazenyl)naphthalene-1-sulfonate **(6h)**

Red, m.p> 300 ^{o}C; R_f: 0.52 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3562 (br), 3055, 1705, 1628, 1588, 1462, 1190, 1064, 865, 822, 639 cm^{-1}. ^{1}H-NMR (DMSO 300 MHz) δ (ppm): 7.93 (d, 4H, 7Hz, Ar-H), 7.60 (d, 4H, Ar-H, 7.5 Hz), 7.48 (d, 2H, 7.3Hz, Ar-H), 7.56 (d, 2H, 7.2 Hz, Ar-H), 7.77 (t, 2H, 7Hz, Ar-H), 7.82 (t, 2H, 7Hz Ar-H), 6.2 (s, 2H, Ar-H), 6.3 (d, 2H, Ar-H, 7.1Hz), 7.0 (d, 2H, Ar-H, 7.1Hz), 6.8 (br s, 4H); Anal. Calcd. For $C_{44}H_{28}N_8O_{10}S_2Na_2$: C, 56.28; H, 2.98; N,11.94; S, 6.82; Found: C, 56.10; H, 2.88 N,11.85; S, 6.90.

Sodium 4-((E)-(3-carboxy-4-hydroxyphenyl)diazenyl)-3-((E)-(4'-((E)-(1-((E)-(3-carboxy-4-hydroxyphenyl)diazenyl)-4-sulfonatonaphthalen-2-yl)diazenyl)-[1,1'-biphenyl]-4-yl)diazenyl)naphthalene-1-sulfonate **(6i)**

Brownish red, m.p> 300 ^{o}C; R_f: 0.48 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3510 (br), 3065, 1735, 1623, 1585, 1448, 1208, 1060, 875, 812, 680 cm^{-1}.^{1}H-NMR (DMSO 300 MHz) δ (ppm): 7.973 (d, 4H, 7Hz, Ar-H), 7.654 (d, 4H, Ar-H, 7.5 Hz), 7.53 (d, 2H, Ar-H, 7.3Hz,), 7.58 (d, 2H, 7.2 Hz, Ar-H), 7.70 (t, 2H, 7Hz, Ar-H), 7.81 (t, 2H, 7Hz Ar-H), 6.9 (d, 2H, Ar-H 7.3 Hz), 7.4 (d, 2H, Ar-H 7.3 Hz), 8.0 (s, 2H), 6.8 (br s, 2H), 11.00 (s, 2H); Anal. Calcd. For $C_{46}H_{28}N_8O_{12}S_2Na_2$: C, 55.53; H, 2.816; N,11.26; S, 6.43; Found: C, 55.40; H, 2.78; N,11.10; S, 6.35.

Sodium 4-((E)-(4-hydroxyphenyl)diazenyl)-3-((E)-(4'-((E)-(1-((E)-(4-hydroxyphenyl)diazenyl)-4-sulfonatonaphthalen-2-yl)diazenyl)-[1,1'-biphenyl]-4-yl)diazenyl)naphthalene-1-sulfonate **(6j)**

Brownish red, m.p> 300 ^{o}C; R_f: 0.56 (ethyl acetate: ethanol 1: 1); FTIR (Neat) ν: 3550 (br), 3070, 1715, 1623, 1434, 1230, 1055, 870, 818, 665 cm^{-1}.^{1}H-NMR (DMSO 300 MHz) δ (ppm) : 7.94 (d, 4H, 7Hz, Ar-H), 7.67 (d, 4H, Ar-H, 7.5 Hz), 7.52 (d, 2H, Ar-H, 7.3Hz,), 7.55 (d, 2H, 7.2 Hz, Ar-H), 7.73 (t, 2H, 7Hz, Ar-H), 7.88 (t, 2H, 7Hz Ar-H), 6.9 (d, 2H, Ar-H 7.3 Hz), 7.4 (d, 2H, Ar-H 7.3 Hz), 7.1 (d, 4H, Ar-H,7.3Hz), 6.7 (d, 4H, Ar-H,7.3Hz), 6.4 (br s, 2H,O-H); Anal. Calcd. For $C_{44}H_{28}N_8O_8S_2Na_2$: C, 58.27; H, 3.09; N, 12.36; S, 7.064; Found: C, 58.15; H, 3.04; N, 12.23; S, 7.012.

Results and Discussion

Synthesis of Dyes **6a-j**

Synthesis of Congo red dye and its derivatives (**6a-j)** was achieved in excellent yields, according to the synthetic strategy outlined in scheme 1 starting from benzidine (**1**). Congo dye (**4**) was freshly prepared by diazotization of benzidine at 0-5^{o}C with nitrous acid generated in situ by the reaction of sodium nitrite and hydrochloric acid. Sodium naphthionate (**3**) was connected with diazo of benzidine (**2**) at low temperature, which was maintained throughout the completion of coupling reaction. The pH of reaction was maintained at 8.0 and the completion of the reaction was monitored by taking TLC of reaction mixture in ethyl acetate: ethanol 1:1 system. The dye was salted out from 20% solution of sodium chloride and dried at 70^{o}C.

Next the diazotization of dye (**4**) with sodium nitrite and hydrochloric acid at 0-5^{o}C followed by coupling with different coupling partners like H-Acid, Gamma Acid, Schaeffer acid, 2-naphthol, phenylmethyl pryazolone, *p*-sulfophenylmethyl pyrazolone, resorcinol, phenol, salicylic acid, and 2, 4-diaminobenzene sulfonic acid was achieved at pH above 8.0. On completion of reaction Congo red dye derivatives **6a-j** were separated by salting out or by simple filtration. Dyes in which coupler carried no any solubilizing groups

such as sulphonic and carboxylic were separated by filtration through filter paper. The structures of couplers **5a-j** and those of new synthesized dyes **6a-j** are shown in Fig. 1 and 2 respectively.

Characterization of Dyes **6a-j**

Synthesized dyes have been characterized by UV-Visible, FTIR and NMR to confirm the compounds. UV-Visible provided the information either the conjugation has been increased in the derivatives **6a-j,** from the parent compound 4 or not. The absorption maxima (λ_{max}) of the dyes **6a-j** were recorded in water and are shown in Table-1 (Fig. 3). The λ_{max} values are directly related to the nature, electronic power and position of the substituents on the aromatic rings of the coupler motif as well as the diazo component. These dyes show two absorption maxima, one of them in the UV range due to π-π^* transition of the C=C present in the aromatic moiety of dyes common in all dyes. Similarly, there is another absorption maxima, which lies in the visible region, and is due to π-π^* transition of azo linkage N=N of dyes and these transitions are responsible for their yellowish red colour. All dyes have same chromophoric functionalities, but the difference is of coupling components. These couplers affect the λ_{max} of dyes, depending upon the functional groups attached at couplers and it is highest for dye **6i**

The infrared spectra of the Congo red derivatives **6a-j** exhibited absorption peaks due to stretching and bending vibrations of O-H, N-H, Ar-H, C-H, C=O, C=C, SO_3H, and N=N at 3400-3500, 3160- 3000, 2929, 1700-1760, 1660,1590, 1502, 1070, 723, 672 cm^{-1} respectively as depicted from their FTIR spectra. Specifically speaking, using FTIR spectrum of 6a, 6d, 6h and 6i showed broad broads in the range 3200-3500 cm^{-1} which is due to H-bonding of OH and COOH groups present couplers. The stretching peaks of N-H groups have been masked due to the broadness of band which is present in H-acid coupler. A peak is observed at 1739 cm^{-1} in dye **6i** due to the C=O functionality of salicylic acid. The absorption peak at 1581 and 1513cm^{-1} showed the presence of C=C stretching vibrations of aromatic nuclei in the coupler as well as diazo component of dye **6i**. Azo linkage is established by the presence of peak at 1482cm^{-1} and is present in FTIR spectra of all compounds. The stretching peak of C-O bond is present at 1042 cm^{-1} (figure 4). A broad, prominent peak at 1200-1250 cm^{-1} is seen in all dyes (**6a-j)** for S=O stretching vibrations due to presence of SO_3H group.

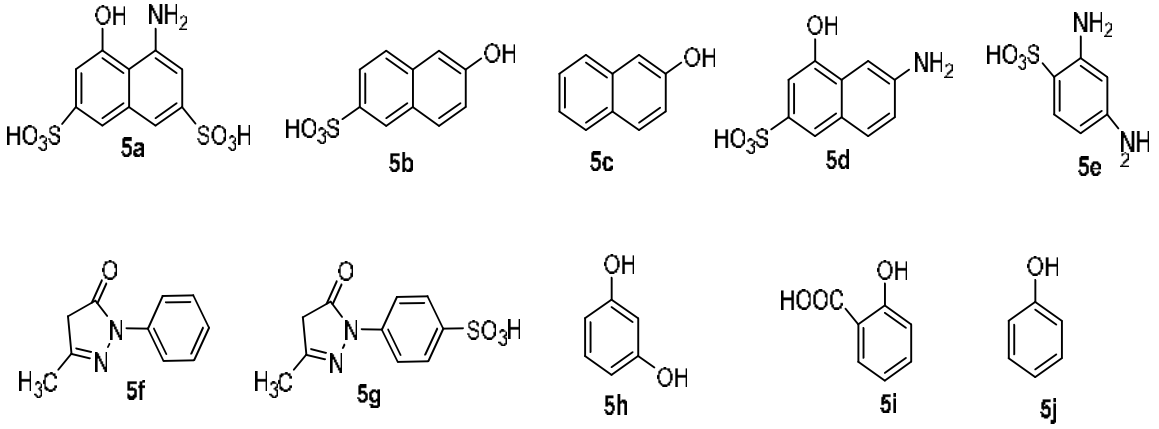


Fig. 1: Structures of the couplers 5a-j used inthe synthesis of Cong Red derivatives.

Table-1: U.V Visible absorption wavelengths of Congo derivatives **(6a-j)**

S.No.	λ_{max}
6a	487
6b	510
6c	507
6d	495
6e	498
6f	504
6g	524
6h	502
6i	544
6j	513

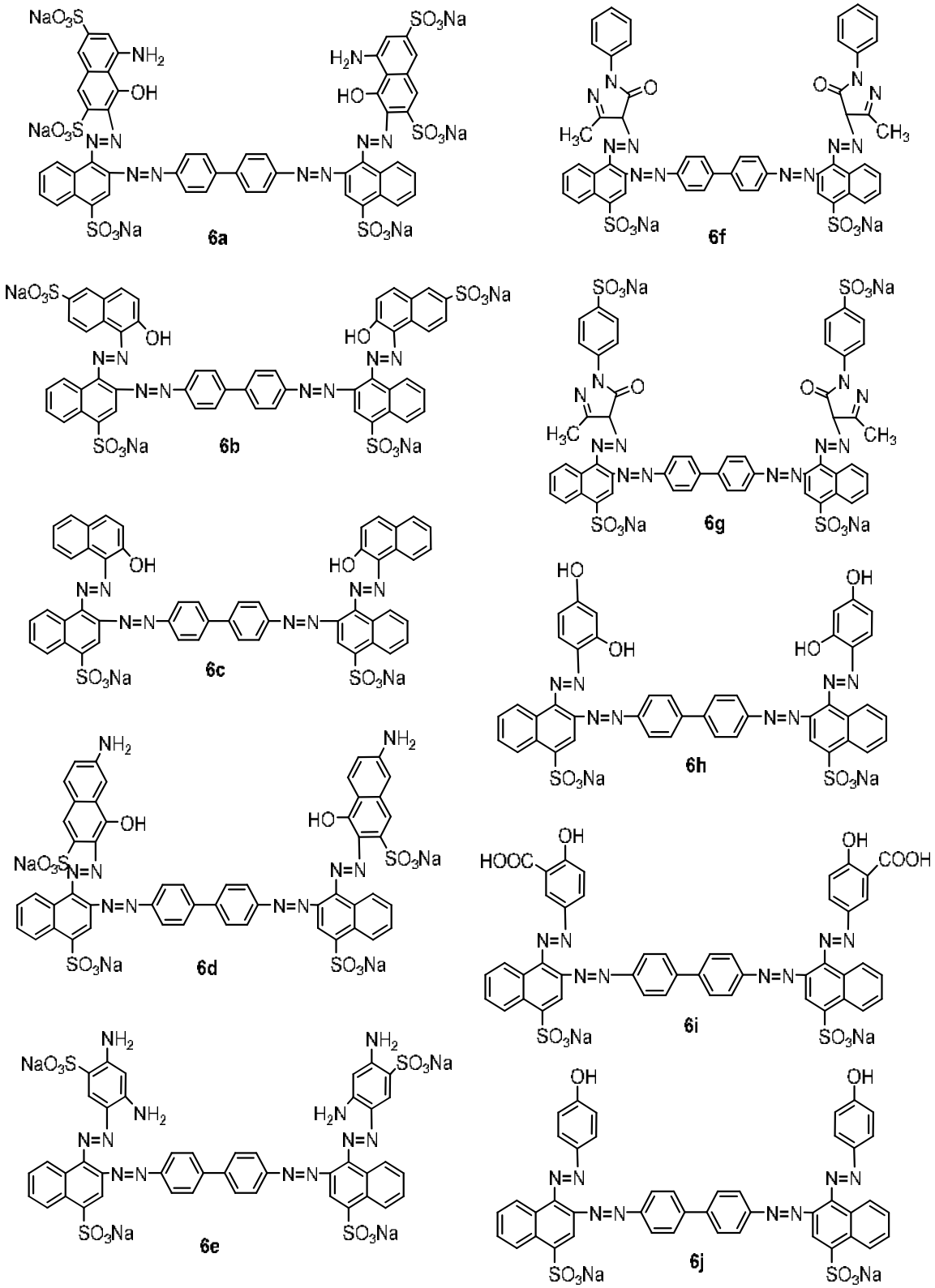


Fig. 2: Structures of Congo Red dye derivatives **6a-j**.

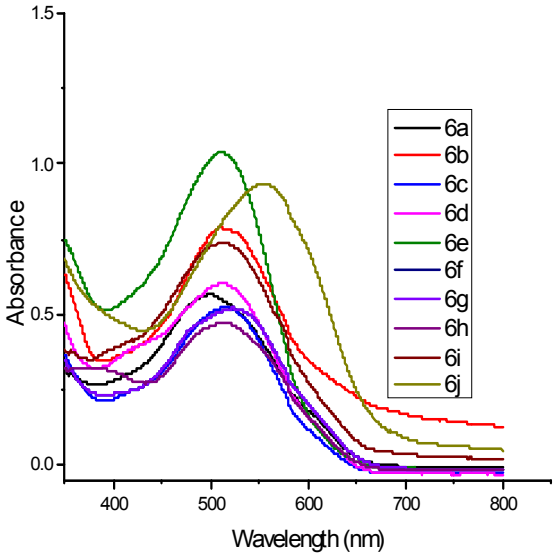


Fig. 3**:** U.V Visible spectra of congo red derivative **6a-j.**

In **6f** and **6g** peak at 3200-3500 cm^{-1} is absent, indicating the lack of carboxylic or hydroxyl groups present in these derivatives. Carbonyl group is indicated by the peak at 1730 cm^{-1} in both dyes. In **6b, 6c** and **6j** exhibited the peaks in the range 3400-3600 cm^{-1}due to hydroxyl group in these derivatives. In this way functional gropus in all dyes (**6a-j**) have been confirmed from their respective FTIR spectra [19].

From the ^{1}H-NMR spectra of dyes **6a-j** common peaks in the range 6.645-7.90 ppm are observed due to presence of aromatic nuclei congo red precursor and difference in dyes arises due to couplers attached to congo nucleus. In dye 6a six aromatic protons are seen at 7.75-7.92 ppm while N-H and O-H protons are present at 4.0 and 6.3ppm respectively. Dye 6b showed signals down field due to ten aromatic protons of schaeffer acid coupler at 7.0- 8.3ppm and O-H peak at 6.7ppm. In dye 6c 12H multiplet peaks are present in the aromatic region due to β- Naphthol coupler and dye 6d represented 8H multiplet peaks because of aromatic protons groups present in the coupler in the aromatic region of the TMS scale. Dye 6e showed peaks due to 4H aromatic, 8H, NH_2 and 2O-H peaks at positions 5.9-7.4, 4.8 and 6.0 ppm respectively. In case of dyes 6f and 6g at 2.4-2.45 ppm peaks are attributed to CH_3 proton present in these dyes, 10H and 8H multiplet peaks are present at 7.24-7.46 and 7.90-7.95ppm respectively. In dye 6h, 2H-singlet, 2H-doublet and 2H are observed at 6.2, 6.3 and 7.0ppm aromatic protons and in dye **6j,** two 4H-doublet peaks are obvious at positions 6.7-7.1ppm and at 6.4ppm O-H shifts are present. The dye **6i** exhibited signals for aromatic protons in the range 6.64-8.37ppm. The carboxylic group in dye 6i is confirmed from broad downfield singlet signal at 15.10ppm (Figure 5).

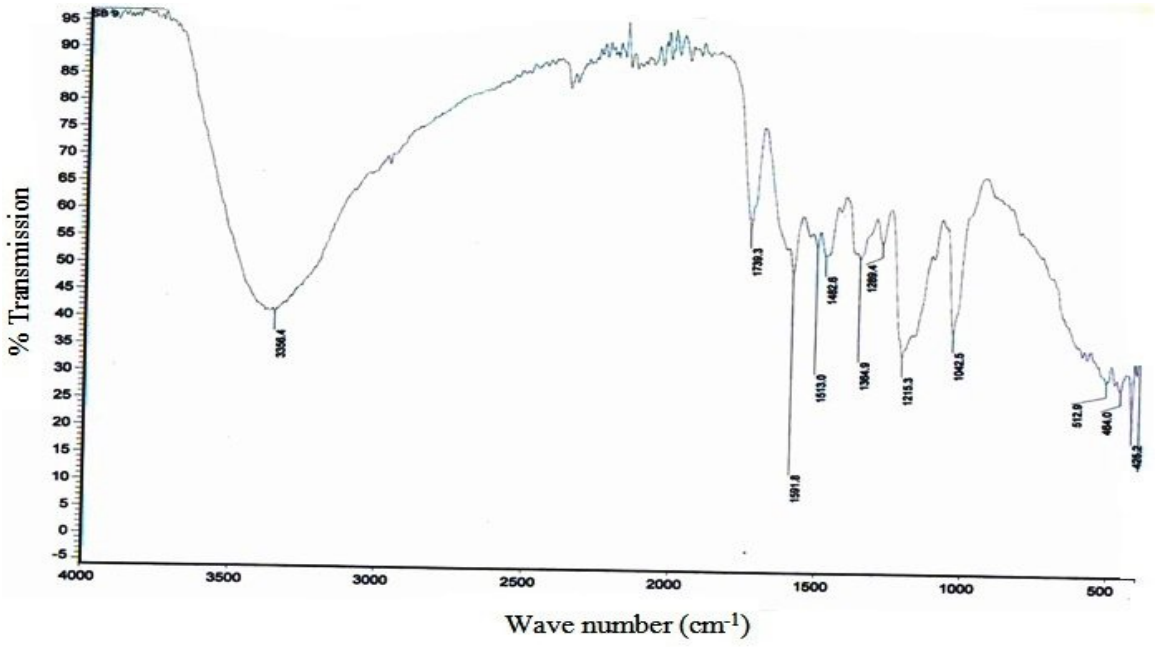


Fig. 4: FTIR spectrum of Congo red dye derivative **6i.**

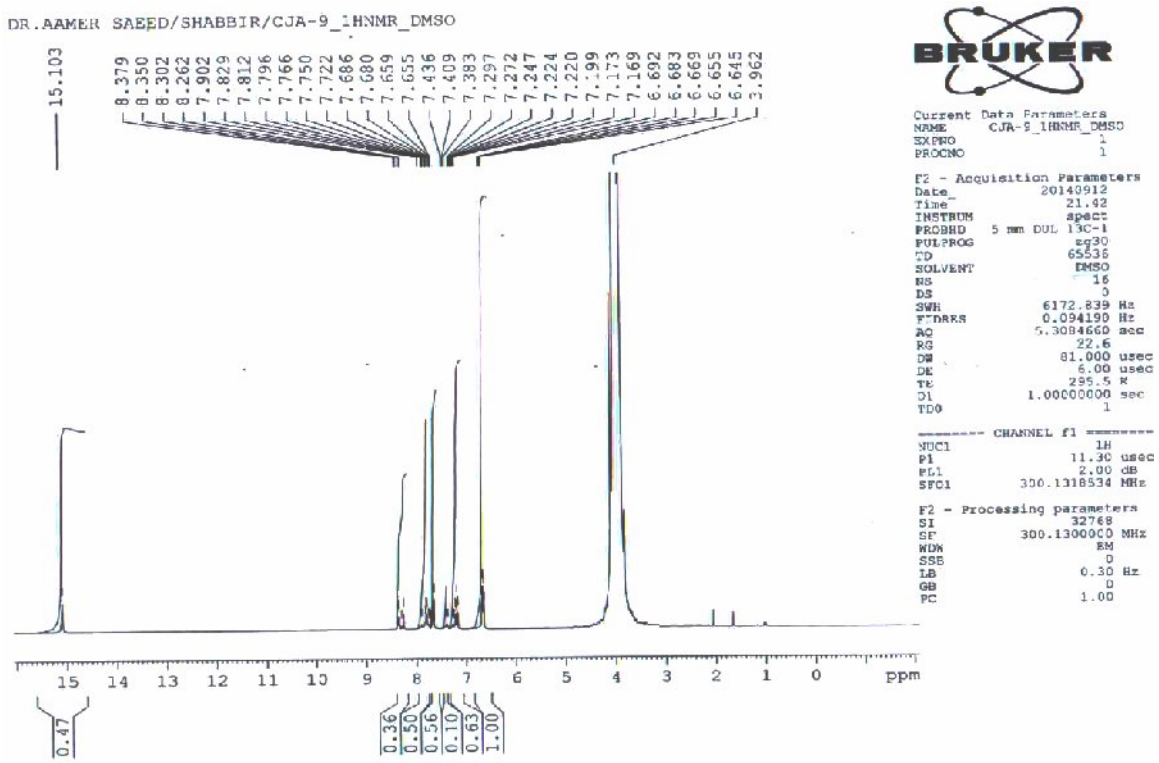


Fig. 5: ^{1}H-NMR spectrum of Congo red dye derivative **6i.**

Table-2: Ion Trapping capacity of Synthesized Congo Red Dye Derivatives from Hard Water of total Hardness 650 ppm

Dye	Dye Solution	Hard water (650ppm)	ml of 0.05M EDTA solution used	Total Hardness (ppm)
6a	**5ml**	**10ml**	**0.78**	**390**
6b	**5ml**	**10ml**	**0.75**	**375**
6c	**5ml**	**10ml**	**0.80**	**400**
6d	**5ml**	**10ml**	**0.90**	**450**
6h	**5ml**	**10ml**	**0.90**	**450**
6i	**5m**	**10ml**	**0.70**	**350**

$$\text{Total Hardness (ppm)} = \frac{\text{Molarity of EDTA x Formula Weight of } CaCO_3 \text{ x ml of EDTA Solution x 1000}}{\text{ml of Hard Water Solution}}$$

Applications of Dyes as Water Softeners

Hard water is recognized by the presence of calcium and magnesium ion in higher concentration. These ions are present in water in the form of salt like carbonates, bicarbonates, chlorides and sulfates. Carbonates and bicarbonates are source of ordinary hardness of water while chlorides and sulfates cause permanent hardness. Ordinary hardness can be removed just by boiling the water and then filtration to remove suspended particles, while permanent hardness cannot be removed unless proper treatment is given. These both kinds of hardness are dangerous for systems where water is being used in bulk quantity and for longer times like boilers, cooling towers, water coolers etc. These dyes **6a-j** were assessed for sequestering the calcium and magnesium ions in hard water, while the dyes **6a-d** and **6h-i** were proved beneficial in this regard. The following equation was used to determine the hardness of water without dyes and Congo red dye derivatives [20].

Hard water (10ml) of 650 ppm was treated with 5ml of an aqueous solution (600ppm) of dyes 6a-d and 6h-i. Ion pick up capacity of these dyes is shown below in Table-2. Eriochrome black T and ammonia buffer of pH=10 were used during the hardness analysis of hard water.

Dye **6i** was found to be excellent in trapping the ions in hard water, because of the capability of COOH and OH in the coupling component of dyes ortho to each sides of dye as shown in structure. Similarly, other dyes have amino and hydroxyl groups ortho to azo linkage. So these dyes are capable of establishing coordination linkages with calcium and magnesium ions.

Boiler water treatment formulation can be made from these dyes to remove hardness of water. Similarly, during application of dyes on fibers, EDTA, NTA and Calgon are added as sequestrants, while using these dyes these chemicals will not be added.

Conclusions

Synthesis of new Congo red dye **6a-j** derivatives has been achieved by diazotization of Congo red dye with various couplers **5a-j**. The synthesized dyes especially those having a carboxylic and hydroxyl groups ortho each other in the coupling partners, were shown to be efficient in hardness reduction in hard water.

References

1. J. O. Otutu, Synthesis of Some New Disperse Dyes Derived from N-phenyl Naphthylamine. *Orient. J. Chem.,* **27**, 1011 (2011).
2. B. Kirkan and R. Gup, Synthesis of New Azo Dyes and Copper (II) Complexes Derived from Barbituric Acid and 4-aminobenzoilhydrazone, *Turk. J. Chem.,* **32**, 9 (2008).
3. A. S. Shawali and M. A. N. Mosselhi, Hydrazonoyl Halides: Useful Building Blocks for the Synthesis of Aryl Azoheterocycles, *J. Hetero. Chem.,* **40**, 725 (2003).
4. R. Gup, E. Giziroglu and B. Kirkan, Synthesis and Spectroscopic Properties of New Azo-Dyes and Azo-Metal Complexes derived from Barbituric Acid and Aminoquinoline, *Dyes.Pigm*, **73**, 40 (2007).
5. E. Yildiz and H. Boztepe, Synthesis of Novel Acidic Mono Azo Dyes and an Investigation of Their Use in the Textile Industry, *Turk. J. Chem.,* **26**, 897 (2002).
6. J. J. Amer, Synthesis and Characterization of 4-(4-Nitrobenzeneazo)- 3-Aminobenzoic Acid Complexes with Y (III) and La (III) ions, *Eur. Chem. Bull.,* **2**, 383 (2013).
7. M. S. Hemang, K. S. Yogesh, R. S. Ashish, S. R. Dilipsinh, I. S. Amish and J. S. Purvesh, Azo Group Containing Bis Ligand and its Coordination Polymers. *Chem. Sci. Trans.,* **2**, 301 (2013).
8. B. V. Girish and V. Z. Raksha, Synthesis and Analytical Studies of Some Azo Dyes as Ligands and Their Metal Chelates, *Inter. J. Chem. Sci.,* **9**, 87 (2011).
9. Y. Emel and B. Hamit, Synthesis of Novel Acidic Mono Azo and an Investigation of their Use in the Textile Industry, *Turk. J. Chem.,* **26**, 897 (2002).
10. H. G. Garg and C. Praksh, Preparation of 4-arylazo-3,5-disubstituted-(2*H*)-1,2,6-thiadiazine-1,1-dioxides, *J Medic. Chem.,* **15**, 435 (1972).
11. C. H. Browing, J. B. Cohen, S. Ellingworth and R. Gulbransen, The Antiseptic Properties of the Amino Derivatives of Styryl and Anil Quinoline, *J. Storage.*, **100**, 293 (1926).
12. U. Pagga and D. Brown, The Degradation of Dyestuffs in Aerobic Biodegradation Tests, *Chemosphere.*, **15**, 479 (1986).
13. C. Park, J. Lim, Y. Lee, B. Lee, S. Kim, J. Lee and S. Kim, Optimization and Morphology for Decolorization of Reactive Black 5 by Funalia trogii, *Enz. Micro. Technol.,* **40**, 1758 (2007).
14. G. M. Rajendra, S. V. Madhu and K. S. Naveen, Voltammetric Investigations of the Reduction of Direct Orange-31 a bisazo dye, *Croatica. Chemica. Acta.,* **71**, 715 (1998).
15. Olayinka, O. A., E. A. Oluwabunmi, O. A. Alice, E. Abiola. And U. A. Winifred, Synthesis and Spectroscopic Study of Naphtholic and Phenolic Azo Dyes, *Phys. Rev. Res. Inter.,* **3**, 28 (2013).
16. G. Chandravadivelu and P. Senniappan, In-Vitro Antimicrobial Activity of Novel Derivative of Azo Dye from Cyano Ester, *Inter. J. Pharma. Chem. Res.,* **1**, 1082 (2011).
17. P. S. Patel, Studies on Synthesis and Dyeing Performance of Disperse Azo Dyes Based on Schiff Base of Ninhydrin and 3-amino phenol, *Arch. Appl. Sci. Res.,* **4**, 846 (2012).
18. A. Khalid, M. Arshad and D. E. Crowley, Accelerated Decolorization of Structurally Different Azo Dyes by Newly Isolated Bacterial Strains, *App. Micro. Biotech.,* **78**, 361 (2008).
19. B. H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications.* John Wiley & Sons, Ltd., ISBNs: 0-470-85427-8 (2004).
20. D. A. Skoog, D. M. West,F.J. Holler and S.R. Crouch, *Introduction to Analytical Chemistry,* 8th Ed., Cengage Learning Asia Pte Ltd., p. 372 (2012).