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Cyclic Voltammetry and Thermal Degradation of Novel 3, 4-aminophthalic acid azo dyes as Antibacterial agents

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Abstract

A convenient systematic approach for the preparation of biologically potent 3,4-aminophthalic acid azo dyes **5(a-f)** for the synthesis of intermediate aminophthalic acid, from starting material such as phthalic anhydride. Phthalic anhydride upon nitration at appropriate experimental conditions yields to 3,4-NPA and these were separated purified and characterized. These NPA's were reduced to the corresponding APAs in presence of aqueous $Na_2S_9H_2O$ as reducing agent at controlled reaction conditions. Efforts are made to isolate these aminophthalic acids were unsuccessful hence, an in-situ preparation of series of 3-hydroxy-2-naphthoic acid derivatives by dia-zotization coupling to achieve target compounds **5(a-f)**. The molecular formula, molecular weight, molecular structure, solubility, colour and yield were reported in **Table 2**. The IR spectra, NMR spectra and Mass spectra of these compounds are given in fig's 1-6, 7-19, and 20-21 respectively. The newly synthesized azo dye compounds were screened for there *in-vitro* antimicrobial activity.

Keywords: Amino phthalic acid; Azo dyes; Thermal characterization; Antimicrobial

1. Introduction:

Phthalic anhydride (isobenzofuran-1, 3-dione), was discovered in 1836 by A. Laurent, and it is produced commercially since from 1872 when BadischeAnilin and Soda-Fabrik **(**SFBA) was developed during the oxidation process of naphthalene [1]. Phthalic anhydride is the first anhydride of a dicarboxylic acid is used commercially as like acetic acid. Phthalic anhydride is colourless needles, with a monoclinic or rhombic crystalline nature with very essential starting materials for dyes and polymer industries [2,3].

Phthalein, anthraquinone, indanthrene, phthalocyanine and rhodamine dyes which have been synthesized using phthalic acid and its derivatives since from 100 years and still they are very important intermediates for many organic synthesis.

Naphthalene chemistry started by Erlenmeyer in the 1866. The structural evidence for the chemical naphthalene and its derivatives of mono, dinitro and 2-naphthalamine was published in 1888[4]. In nineteenth century, novel naphthalene derivatives were synthesized as part of azo dye compounds. The fundamental components were generated during that time was played an very important role even till today[4,5]. From naphthalene derivatives azo compounds and pigments has been the leading outcomes.

According to indexes of colour point out 270 contrary naphthalene derivatives as a prime to colouring agents [6]. A standard procedure for reduction, amination, sulfonation, hydroxylation and nitration, a range of naphthalene compounds were synthesized in the coming years [7-11]. The agrochemical and pharmaceutical field found effective in achievement of novel naphthalene compounds [12]. Naphthalimides were examined in a various method to analyse as dye intermediates are applied on artificial, natural textiles and other polymeric materialsas well. Pioneering work on naphthalimide derivatives also supports their role as intermediates for dye stuffs preparation [13-17]. Hetero compounds like 1, 8-naphthalic anhydrides, phenylazophthalimides and naphthlimides are considered for the production of dyes [18, 19] for other polymer fibers, polymeric materials and capable of copolymerization. A benzene azonaphthalimide dye is a derivative of 4-amino naphthalimide had individual intense colour [20]. The necessary actions and significant attention have been faded the effect of dye operation on environment through diminution in outflowing and in the usage of energy as well as materials [21, 22].

2. Materials and methods:

2.1. General: IR spectra of the compounds were recorded on a SHIMADZU FT-IR 8400s spectrometer by KBr pellet method. The NMR including proton and carbon were verified in deuterated dimethyl sulfoxide on amx400 FT-NMR spectrometer at 400 MHz using tetramethylsilane (TMS) as reference. LC-MSD-trap-XCTplus mass spectrometer was used to record mass spectrum. The UV-Visible spectra were documented in DMSO, DMF, MeOH, acetone, AcOH, THF and 1N NaOH, in SHIMADZU UV-Visible 1650 spectrometer. SHIMADZU TA-60WS thermal analyzer was used to carried out the thermal analysis in air at 5 ^{o}C min^{-1}. Electro analyzer-201 Cyclic voltammetry was used to record electro chemical and redox properties of dyes in department of Chemistry, Kuvempu University.

2.2. Nitration:

2.2.1. Synthesis 3 & 4 nitrophthalic acid (*3-NPA & 4-NPA*)

Method A: Phthalic anhydride (1) 100 g (0.675 ml) and conc. H_2SO_4 100 ml was placed in three necked round bottom flask (500 ml) suspended in a water bath, with an addition funnel, a thermometer and stirrer. Reaction mixture was heated until the contents attained the temp of 80 ºC. To this mixture, add fuming nitric acid (*d* 1.5) 42 ml and conc. H_2SO_4 30 ml was added dropwise from additional funnel by adjusting the temperature between 100-110 ºC for an hr. Further, the mixture was heated on the water bath, with constant stirring, for 2 hr and allowed to stand overnight, poured into 300 ml of water, filtered to obtain mixture of 3 & 4 NPA. The mixture of 3 & 4 NPA thus obtained was further separated by stirring this mixture thoroughly with 40 ml of water, in which 4-NPA was completely soluble in water whereas compound 3-NPA remained insoluble in the water and it was separated by simple filtration. Similarly compound 4-NPA was isolated from extracting with diethyl ether. The resulted product crude 3-NPA was further recrystallized from hot water. Yield: 25 % MP: 216-218 ºC [23]

2.2.2. Synthesis of 4-NPA (*2b*)

*Method B:*Finely ground 10 g phthalic anhydride (**1**) was taken in a 250 ml conical flask containing 30 ml of conc. sulfuric acid. To this 21g of finely ground potassium nitrate was added with constant stirring and maintained a temperature of 50 ºC for 2 hrs. The mixture was carefully diluted by adding 40ml water. Then the mixture was extracted with diethyl ether. On evaporation, a mixture of 3 & 4 NPA (**2a &**

2b) were obtained. These were dissolved in a required quantity of boiling water and allowed to stand overnight. The crystallized 3-NPA (**2a**) was separated by filtration. Thus, the separation step was repeated for 3 or 4 times. Pure 4-NPA (**2b**) was obtained by extracting the solution containing 4-NPA (**2b**) with diethyl ether and dried in vacuum over phosphorous pentoxide. Yield: 92 %, MP: 206 ºC [24].

2.3. Reduction:

2.3.1. Synthesis of 3-APA (3a)

3-NPA (**2a**) 2.11 g (0.01 mol) was solubilised in 50 ml of 5 % NaOH and sodium sulphide nonahydrate ($Na_2S.9H_2O$) 1.58 g (0.02 mol) was added and stirred for about one hr at 60 ºC. This reaction mixture was cooled to room temperature (RT), filtered and washed. The filtrate was acidify with HCl and stand for overnight then filtered, the filtrate contains 3-APA (**3a**) free from sulphur impurities [25].

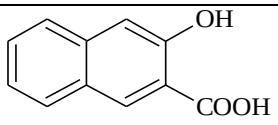
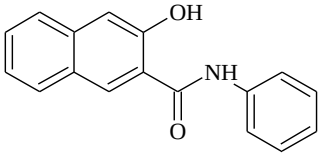
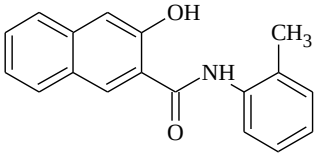
2.3.2. Synthesis of 4-APA (3b)

4-NPA 2.11 g, (0.01 mol) (**2b**) was dissolved in 50 ml of 5% NaOH and Na_2S $9H_2O$ 1.58 g, (0.02 mol) was added and stirred for about one hr at 60 ºC. This mixture was cooled to the RT and filtered. The filtrate was made to acidify with HCl and allowed to stand for 24 hrs and filtered once again to make the filtrate contains 4-APA (**3b**) free from any sulphur impurities [26, 27].

2.4. Coupling components:

The required coupling components were acquired from Aldrich chemicals and they were allowed for purification by recrystallization suing water- ethanol mixture.

Table 1: Name and structure of coupling components

Sl. No	**Name of the Compound**	**Structure**
1	3-Hydroxy-2-naphthoic acid (BONA Acid) (**4a**)	
2	Naphthol-AS (**4b**)	
3	Naphthol-AS D (**4c**)	

2.5. Synthesis of dyes

2.5.1. Synthesis of 4-[(3-carboxy-2-hydroxy-1-naphthyl) diazenyl] phthalic acid (H_2L^1

Diazotization: The filtrate containing 4-APA (**3b**) was allowed to cool at 0-5 ºC, the aqueous sodium nitrite solution ($NaNO_2$, 0.7g 0.01 mol) was added drop wise on constant stirring. After completion of

the addition, continue stirring for 30 min. The excess $NaNO_2$ was removed by adding appropriate quantity of urea.

The *p*H 6 was maintained in the reaction mixture by adding cooled $NaNO_2$ solution. Then the compound **4b** 1.88 g, (0.01 mol), was dissolved in DMF (20 ml), added in portions at 0-5 ºC temperature of *p*H-6 in 2 hrs. The dye compound obtained was filtered, washed, dried, and purified by recrystallization using suitable solvent. The compound synthesized was confirmed by thin layer chromatography (**TLC**). Similar procedure was adopted for synthesizing all other dyes **5(a-f)** by changing their coupling components **4(a-c**) as mention in the

Scheme 1.

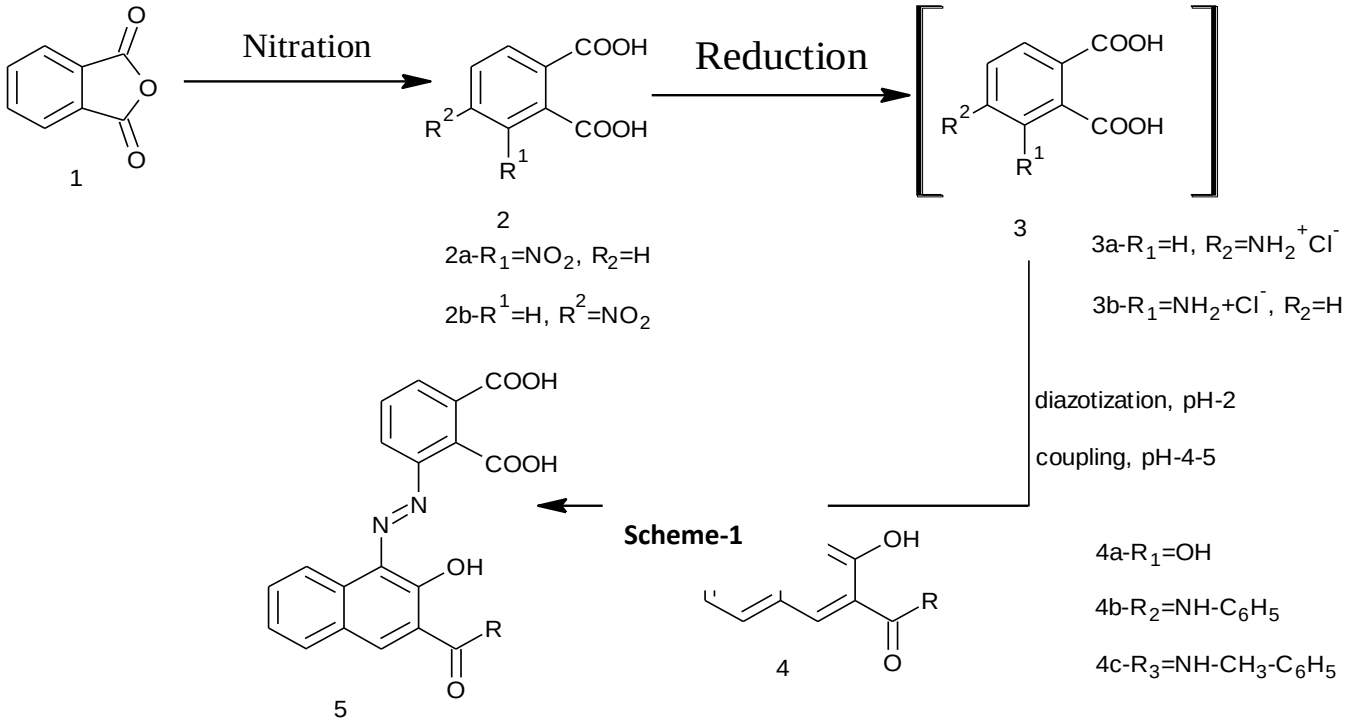
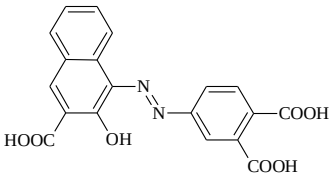
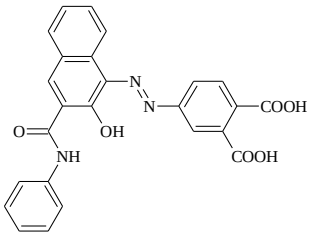
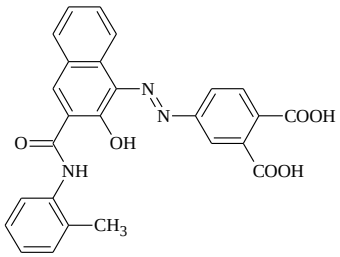
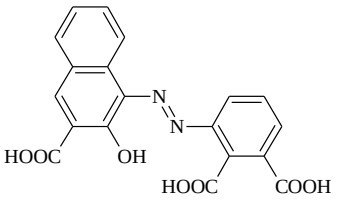
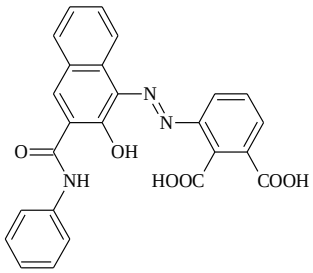
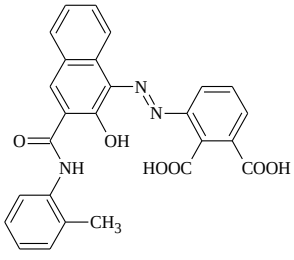


Table 2: Physical characterization structures of dyes 5(a-f)

Dye	Mol. Formula. Mol. Weight	Structure	Colour Appearance	Yield (%)
5a **H_2L^1**	$C_{19}H_{12}N_2O_7$ (380.30)		Brick Red (amorphous)	56
5b **H_2L^2**	$C_{25}H_{17}N_3O_6$ (455.40)		Red (amorphous)	68
5c **H_2L^3**	$C_{26}H_{19}N_3O_6$ (469.43)		Blood Red (amorphous)	62
5d **H_2L^4**	$C_{19}H_{12}N_2O_7$ (380.31)		Orange red (amorphous)	64
5e **H_2L^5**	$C_{25}H_{17}N_3O_6$ (455.40)		Brown (amorphous)	76
5f **H_2L^6**	$C_{25}H_{17}N_3O_6$ (469.43)		Yellow Orange (amorphous)	71

3. Spectral data:

3.1.1. Spectral data of 4-[(3-carboxy-2-hydroxy-1-naphthyl) diazenyl] phthalic acid (5a)

IR(KBr): 3483 cm^{-1}(-OH), 1718 cm^{-1}(-COOH), 1600 cm^{-1}(-N=N-), 1365 cm^{-1}(-C-N=). ^{1}H NMR(DMSO-d_6,ppm): 15.53 (br, s, OH, 1H), 13.03 (br, s, COOH, 3H), 8.63 (s, ArH, 1H), 8.45 (d, ArH, 2H, *J* = 8.03), 7.95 (d, ArH, 1H, *J* = 7.63), 7.87(d, ArH, 1H, *J* = 8.15), 7.74 (t, ArH, 1H, *J* = 7.11, 14.65), 7.54 (t, ArH, 1H, *J* = 7.34, 14.82). ^{13}CNMR (DMSO-d_6,ppm): 171.2, 167.3, 167.3 (COOH), 165.6(C-OH), 144.9, 136.3-123.2(ArC-C), 110.1, (ArC-N).

***Compound 5a*:** IR data of the compound **5a** show a broad band at 3483 cm^{-1} region which can attached with hydroxyl group and a sharp intense band at 1718 cm^{-1} region was corresponds toC=O stretching of the carboxylic acid. The band at 1600 cm^{-1} was correlate to the azo group in the compound (**fig.1**). The ^{1}H NMR spectra of **5a** shows a peak at 13.3 ppm due to carboxylic acid proton, a broad peak at 15.5 ppm for -OH proton, and a multiplet from 6.5 to 8.5 ppm for aromatic proton (Ar-H) (**Fig.9**) respectively. The ^{13}C NMR data of the compound **5a** pretending 3 peaks at δ 171.2, 167.9, and 167.3 ppm due to carbonyl carbon and 165.6 ppm was corresponds hydroxyl carbon atom attached to (C-OH). The peak at 110.1 ppm was assign to carbon attached to the nitrogen atom of the azo group (ArC-N=N). Similarly, the peaks due to aromatic carbons appeared in between 120-140 ppm (**Fig.14**). Similarly structures of all other compounds were established and are given in the experimental section in Table.2.

3.1.2. Spectral data of 4-[(2-hydroxy-1-naphthyl-3-anilide) diazenyl] phthalic acid (5b)

IR (KBr): 3292 cm^{-1}(-NH), 1622 cm^{-1}(-COOH), 1610 cm^{-1}(-N=N-), 1363 cm^{-1}(-C-N=). ^{1}H NMR (DMSO-d_6,ppm): 16.0 (br, s OH), 13.0 (br, s, COOH, 2H), 11.2 (br, s , NH), 8.80 (s, ArH, 1H), 8.47 (d, ArH, 1H, *J* = 7.84), 7.94-8.15 (m, ArH, 4H), 7.71-7.82 (m, ArH, 3H), 7.56 (t, ArH, 1H, *J* = 7.28, 14.40), 7.4 (t, ArH, 2H, *J* = 7.84, 15.69), 7.14 (t, ArH, 1H, *J* = 7.08, 14.22). ^{13}C NMR (DMSO-d_6,ppm): 167.2, 165.6, (COOH), 161.5 (C=O), 153.7 (C-OH), 146.7, 143.3, 131.7-119.8 (ArC), 110.5, (ArC-N).

3.1.3. Spectral data of 4-[(2-hydroxy-1-naphthyl-toluidine) diazenyl] phthalic acid (5c)

IR(KBr): 3326 cm^{-1}(-OH), 3292 cm^{-1}(-NH), 1637 cm^{-1}(-COOH), 1589 cm^{-1}(-N=N-), 1348 cm^{-1}(-C-N=). ^{1}H NMR(DMSO-d_6,ppm): 16.1 (br, s, OH, 2H), 11.2 (br, s, NH, 1H), 8.94 (s, ArH, 1H), 8.45 (d, ArH, 1H, *J* = 7.98), 8.19 (d, ArH, 1H, *J* = 7.89), 7.99-8.08 (m, ArH, 2H), 7.76 (t, ArH, 1H, *J* = 6.68, 14.16), 7.56 (t, ArH, 1H, 7.31), 7.17-7.34 (m, ArH, 3H), 7.02-7.12 (m, ArH, 2H), 2.3 (s, CH_3, 3H).^{13}C NMR (DMSO-d_6,ppm): 164.5, 165.6, (COOH), 161.5 (C=O), 153.5 (C-OH), 136.3-118.5 (ArC), 110.5 (ArC-N), 17.7 (CH_3). MS: m/z: 470.

3.1.4. Spectral data of 3-[(3-carboxy-2-hydroxy-1-naphthyl) diazenyl] phthalic acid (5d)

IR(KBr): 3525 cm^{-1}(-OH), 1675 cm^{-1}(-COOH), 1595 cm^{-1}(-N=N-), 1332 cm^{-1}(C-N) ^{1}H NMR (DMSO-d_6,ppm): 15.53 (br, s, OH, 1H,), 13.03 (br, s, COOH, 3H), 8.63 (s, ArH, 1H), 8.45 (d, ArH, 2H, *J* = 8.03), 7.95 (d, ArH, 1H, *J* = 7.63), 7.87 (d, ArH, 1H, *J* = 8.15), 7.74 (t, ArH, 1H, *J* = 7.11, 14.65), 7.54 (t, ArH , 1H, *J* = 7.34, 14.82). ^{13}C NMR (DMSO-d_6,ppm): 171.5, 167.5, 165.4 (COOH), 151.0 (C-OH), 145.2, 142.3 (ArC-C), 134.1-121.8, (ArCH), 117.1, (ArC-N).

3.1.5. Spectral data of 3-[(2-hydroxy-1-naphthyl-3-anilide) diazenyl] phthalic acid (5e)

IR (KBr) 3431cm^{-1} (-OH),3299 cm^{-1}(-NH), 1637 cm^{-1} (-COOH), 1595 cm^{-1}(-N=N-), 1361cm^{-1}(-C-N=). ^{1}H NMR(DMSO-d_6,ppm): 11.5 (br, s, OH 1H), 10.6 (br, s, NH 1H), 8.51 (s, ArH, 1H), 7.93 (d, ArH, 1H, *J* = 8.00), 7.76 (d, ArH, 4H, *J* = 7.33), 7.52 (t, ArH, 1H, *J* = 7.04, 14.41), 7.31-7.43 (m, ArH, 5H),

7.15 (t, ArH, 1H, *J* = 7.37, 14.72). ^{13}C NMR ((DMSO-d_6,ppm): 164.5, 165.6, (COOH), 161.5 (C=O), 153.6 (C-OH), 136.3-119.8 (ArCH) 110.4, (ArC-N). MS: m/z: 456, 264 (base peak).

3.1.6. Spectral data of 3-[(2-hydroxy-1-naphthyl-toluidine) diazenyl] phthalic acid (5f)

IR (KBr): 3326 cm^{-1} (-OH), 3292 cm^{-1} (-NH), 1637 cm^{-1} (-COOH), 1589 cm^{-1} (-N=N-), 1348 cm^{-1}(-C-N=). ^{1}H NMR (DMSO-d_6,ppm): 11.8 (s, COOH, 1H), 10.89 (br s, NH), 10.55 (s, OH, 1H), 8.24-8.14 (d, ArH, 1H, *J* = 7.81), 7.9-8.03 (d, ArH, 1H, *J* = 7.802), 7.8-7.74 (d, ArH, 2H, *J* = 8.231), 7.6-7.59 (t, ArH, 1H, *J* = 7.448, 14.84), 7.41-7.33 (d, ArH, 2H, *J* = 11.653), 2.33 (s, CH_3, 3H), ^{13}C NMR (DMSO-d_6): δ(ppm)= 167.5, 165.6 (COOH), 162.5 (C=O), 143.6 (C-OH), 136.3-119.8 (ArCH), 110.4, (ArC-N), 15.1(CH_3).

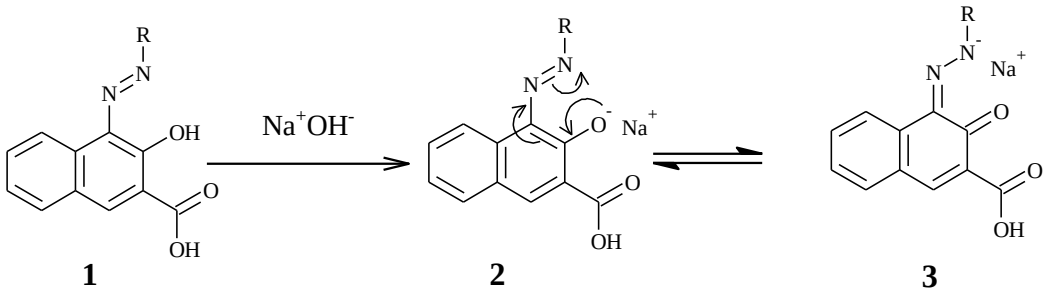
4. Results and Discussion

4.1 Absorption spectral Data

Solvent effect: The absorption spectral data of the compounds **5(a-f)** were registered in diverse solvent medium at a range of 1X10^{-4} to 1X10^{-5} M concentration and the results are statement (Table-3). A characteristic spectrum of **5(a-f)** in MeOH is shown in **fig. 1**. The visible spectra of the dyes were found to possess a strong solvent state, which evidence modification with the opposition of the solvents.

It is accepted that although MeOH, DMSO, DMF, THF, acetone NaOH and AcOH the absorption spectra, $\lambda_{max}$of the dyes alter effectively with change of solvents (e.g. dye **5c**, the λ_{max}: 517, 496 nm in dimethyl sulphoxide, 511 nm in dimethyl formamide, 514, 494 nm in methanol, 495 nm in tetrahydro furan, and 494 nm acetone, 511, 492 nm in acetic acid). λ_{max} of the dyes in NaOH showed marginal shift towards the hypsochromic shift (e.g. for the dye **5c**, λ_{max}: 488 nm in NaOH). Such an effect of solvents is consistent with the phenomena of ionic bonding formation of phenoxide ion is given Scheme-**2**.

In basic solvents, this equilibrium depends on the proton releasing ability of solvents like DMSO and DMF, λ_{max} of the dyes shifted to higher wave length (red shift) due to the formation common anion i.e., inter hydrogen bonding between the solvent and molecule more resonance will be occurred [28-34]. But in case of proton donating solvents such as AcOH and MeOH, λ_{max} is marginally shifted to lower wavelength. The dye **5f** shows hypsochromic shift in almost all the solvents specifically solvents like MeOH, AcOH, and THF the λ_{max} will shift to very lower wavelength region (e.g. for the dye **5f** λ_{max}: 363 nm in MeOH, λ_{max}: 379 nm in acetone, λ_{max}: 382 nm in AcOH).



1 **2** **3**

5a, λmax=504 (acetone) 5a, λ_{max}=460 (NaOH)

Scheme-2

Table 3: Electronic Spectra of 5(a-f) (λ_{max} in nm)

Dye	DMF	DMSO	MeOH	THF	Acetone	1N NaOH	AcOH
5a	512	504	511	503	504	460	521, 502
5b	524	502	517, 496	517, 496	518, 499	441	514, 495
5c	524	502	514, 494	495	494	488	511, 492
5d	508	502, 498	513, 506	516, 499	516, 500	393	519, 499
5e	492	497	511, 494	491 360	491, 360	493	510, 492
5f	460	492	363	401	379	458	382

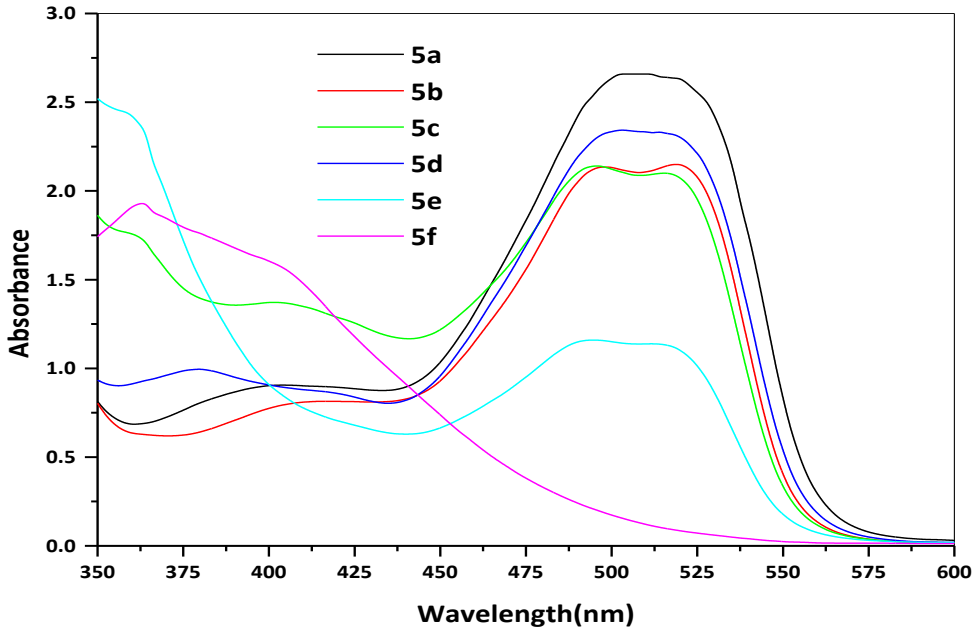


Fig. 1: UV-Visible spectrum of dyes 5(a-f) in MeOH

4.2 Thermal and Kinetic parameters

The thermo analytical parameters curves obtained from TG and DTA study, of all the compounds are summarised in Table 4.The characteristic TG and DTA graphs of the compounds **5(a-f)** is illustrated in fig.2 and 3.

The compound **5a** shows that all the peaks are exothermic and the decomposition occurs in three steps, initial step ranges from 165-205 °C under decomposition temperature of 182 ^{0}C it's an exothermic peak, the second step in the range of 265-330 with decomposition temperature (T_d) was 290 ^{0}C, and the third step occurs in the range of 520-575 ^{0}C and it melts at 547 ^{0}C.

Initial weight loss probably due to absorbed moisture. The weight loss in the first step and loss of 10-12% due to the two -COOH groups present in the phthalic acid followed by the decomposition of azo group leads to cleavage of the molecule finally, phthalic anhydride and naphthoic acid nuclei were decomposes 30% and 45 % respectively were major weight loss. DTA data reveals that the degradation happens in an exothermic manner except compound **5f**. The Broido's method is adopted for evaluating the kinetic and thermodynamic parameters of the compounds [33].

The graph are plots of ln (ln1/Y) versus 1/T (where Y is fraction of the compound undecomposed) was developed against the decomposition portion where the loss of functional groups may cause (fig. 23). From the plots the activation energy (E_a) and frequency (ln A) the Enthalpy (ΔH), Entropy (ΔS) and free energy (ΔG) has been evaluated using standard equation and the results obtained were computed accordingly (Table.5). The TGA studies of dyes, showed that high activation energy is responsible for rapid degradation, whereas low activation energies represent the gradual degradation around their decomposition temperatures.

Table 4: Thermo-analytical data of the dyes 5(a-f)

Dye	Moss loss temp (^{0}C)	DTA $_{max}$ (^{0}C)
5a	165-205	182
	265-330	290
	520-575	547
5b	230-310	254
	500-560	529
5c	220-275	244
	515-560	535
5d	170-245	209
	290-340	307
	470-549	538
5e	240-320	282
	530-580	555
5f	150-190	161
	260-340	299
	490-580	541

Table 5: Kinetic parameters of the dyes 5(a-f)

Dye	Decomposition range (^{0}C)	E_a (kJ mol^{-1})	ln$A$ (s^{-1})	ΔH (kJmol^{-1})	ΔS (kJmol^{-1})	ΔG (kJmol^{-1})
5a	165-205	2.0131	4.5260	-1.7697	-150.61	68.528
	265-330	7.5223	7.2391	2.8415	-146.79	82.645
	520-575	144.89	29.580	138.08	-144.65	118.75
5b	230-310	3.2326	5.2198	-1.1488	-149.3	78.679
	500-560	106.34	24.173	99.677	-143.72	115.36
5c	220-275	0.3658	2.3792	-3.9324	-149.53	77.305
	515-560	119.94	26.186	113.225	-143.68	116.21
5d	170-245	4.3923	5.8813	0.3850	-150.05	72.325
	290-340	6.3421	6.5357	1.5199	-148.10	85.904
	470-549	12.890	7.9714	6.1479	-144.48	117.18
5e	240-320	13.691	8.9337	9.0768	-148.55	82.457
	530-580	86.487	20.755	79.603	-142.31	117.91
5f	150-190	0.8911	3.4003	-2.7171	-151.16	65.601
	260-340	2.5050	4.7344	-2.25059	-148.73	85.072
	490-580	67.710	17.695	60.942	-144.35	117.56

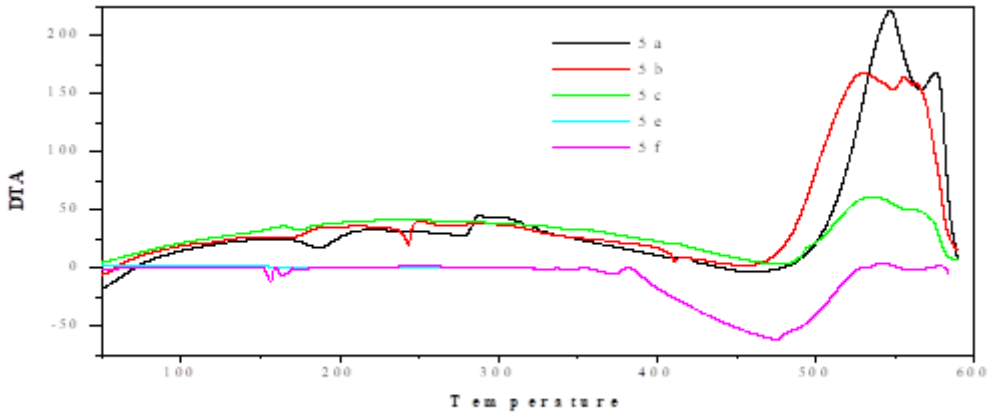


Fig. 2: DTA of Curve 5a-f

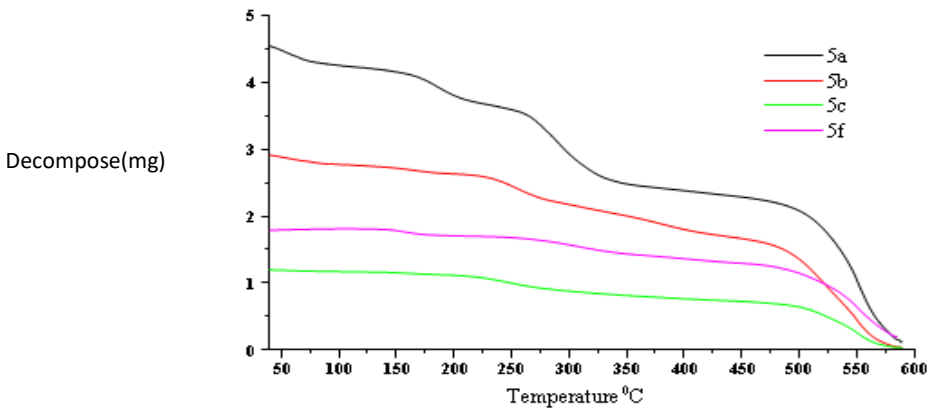


Fig. 3: TGA curve of 5a, 5b, 5c and 5f

4.3 Cyclic voltammetry studies

To obtain the ground state properties and more specifically the mutual donor–acceptor electronic influence, we have studied the redox properties of the 3 and 4-aminophthalic acid azo dyes by cyclic voltammetry.

All the experiments were carried out in Electroanalyzer-201 cyclic voltametry using 0.1M H_2SO_4 as supporting electrolyte and DMF (0.5mM) as a solvent. Electrochemical cell consists of a glass container with a cap having holes for introducing electrodes. Saturated calomel electrode (SCE) is used reference electrode, were platinum foil and glassy carbon are auxiliary and working electrodes respectively. The CV (cyclic voltametric) studies of the compounds was done in -500mV to +500 mV potential range under different scan rates like 25 mV, 50 mV, and 75 mV.

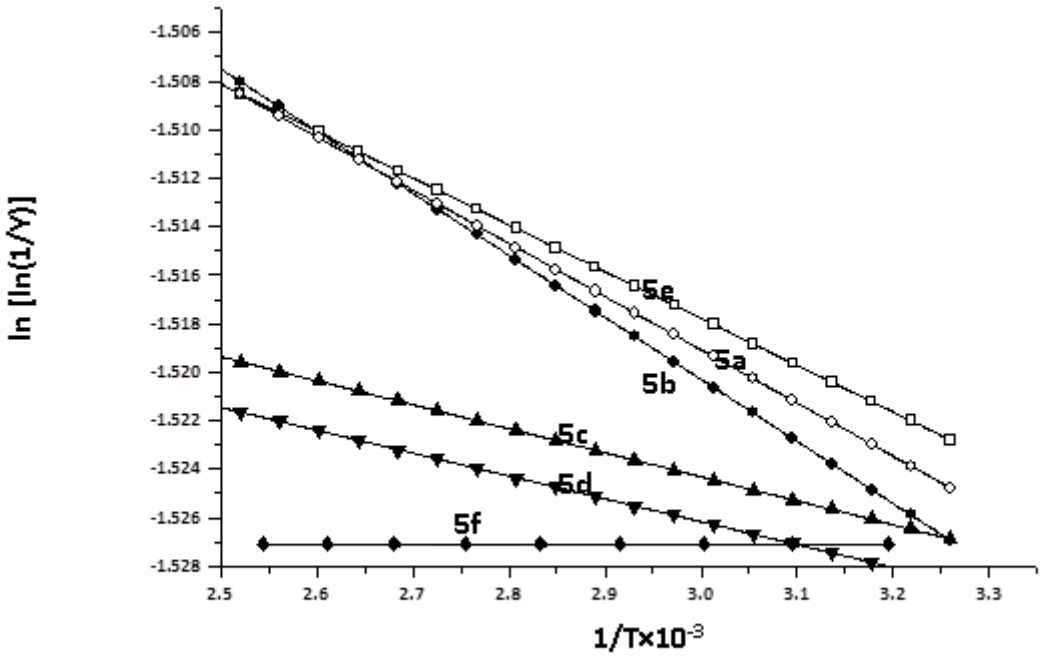
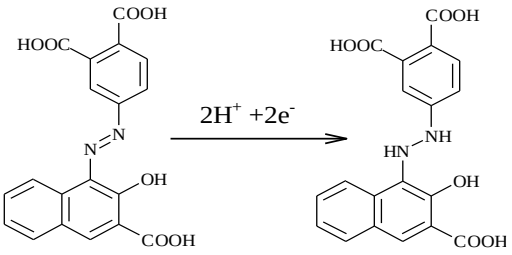


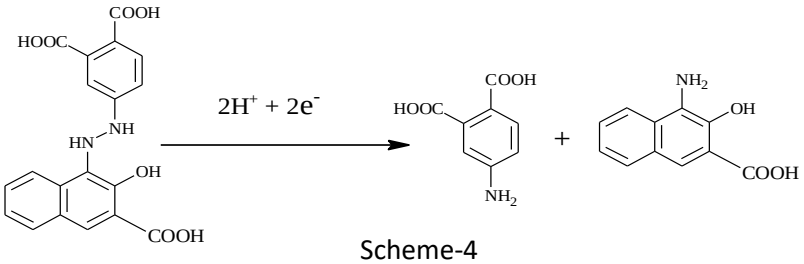
Fig. 4: Plots of ln (ln 1/Y) V/S 1/T thermal degradation of 5a-5f

4.3.1 Reduction of compound 5(a-f)

The reduction results of the compounds **5(a-f)** in a potential range between -421mV to -121mV at *p*H-2 as tabulated in **Table 6** and cyclic voltammogram curves of the dyes **5(a-f)** is showed in fig. 24, 25 and 26. The compound **5a** exhibit one reduction potential in the range-157mV at the scan rate of 50mV and the peak intensity is two electron exchanges. Compound **5b** and **5c** exhibit two reduction potentials, first in the range of -121mV and -155mV and second ranges from -299mV to -334mV under of 50 mV scan rate and the peak intensity is four electron exchanges (Scheme **3**&**4**). In the compound **5a** the withdrawing group –COOH which influence rate of reduction compare **5b** and **5c**. Compounds **5d, 5f** and **5e** exhibit a reduction in a potential range -265mV, -413mV, and -412 mV respectively at 50mV scan rate. The peak intensity of all three compounds shows two electron transfer. The changes in potential **5d** compared to **5f** and **5e** is due to substituent attached to naphthoic acid influences electro transfers [35-37].



Scheme-3

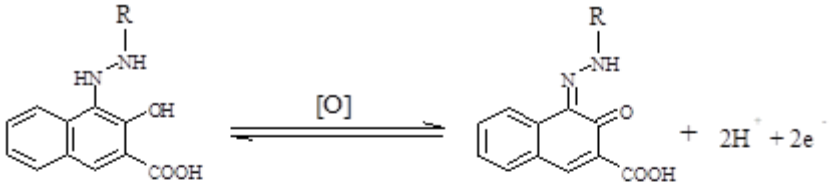


Scheme-4

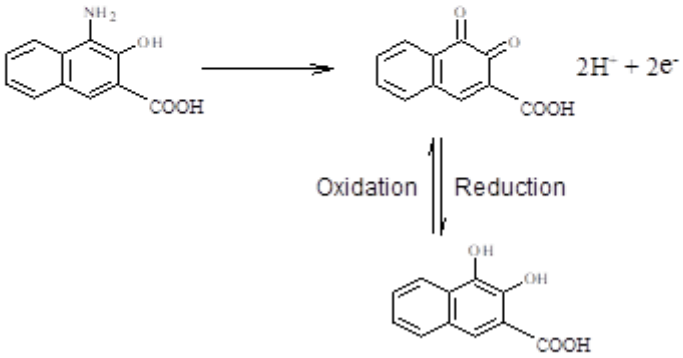
4.3.2 Oxidation potential of dyes 5(a-f)

Oxidation potentialof the compounds **5(a-f)** were showed in a potential range between 344mV to 434mV. The compound **5a and 5d** exhibit one oxidation potential higher range at 410mV and 414 mV at the scan rate of 50mV respectively due influence of -COOH group in ortho position to the -OH group, which influence higher oxidation potential and remaining of all four compounds oxidized in marginal variation in the range of 356mV to 373 mV (Scheme **5**&**6**).

Oxidation:



Scheme-



Scheme-

Table 6: The reduction effects of ring at glassy carbon electrode on diverse scan rates

Dye	Scan rate (mV/s)	E_{pc}(mV)		I_{pc}(µA)		E_{pa}(mV)	I_{pa}(µA)
		E_{pc1}	E_{pc2}	I_{pc1}	I_{pc2}	E_{pa1}	I_{pa1}
5a	25	-152	--	10.07	--	407	-3.31
	50	-157	--	16.38	--	410	-4.43
	75	-173	--	13.72	--	434	-4.58
5b	25	-122	-288	15.55	21.36	355	-10.44
	50	-121	-299	27.29	34.81	363	-13.37
	75	-148	-322	32.46	49.94	365	-24.16
5c	25	-128	-313	15.3	19.85	344	-6.46
	50	-155	-334	22.42	26.67	358	-9.22
	75	-157	-340	24.19	30.53	359	-10.99
5d	25	-243	--	15.51	--	404	-7.63
	50	-265	--	21.21	--	414	-10.4
	75	-265	--	37.14	--	420	-16.72
5f	25	-395	--	22.3	--	367	-6.20
	50	-413	--	27.2	--	373	-10.07
	75	-421	--	40.13	--	369	-12.12
5e	25	-393	--	21.03	--	362	-6.05

	50	-412	--	27.91	--	356	-8.16
	75	-416	--	35.54	--	367	-10.53

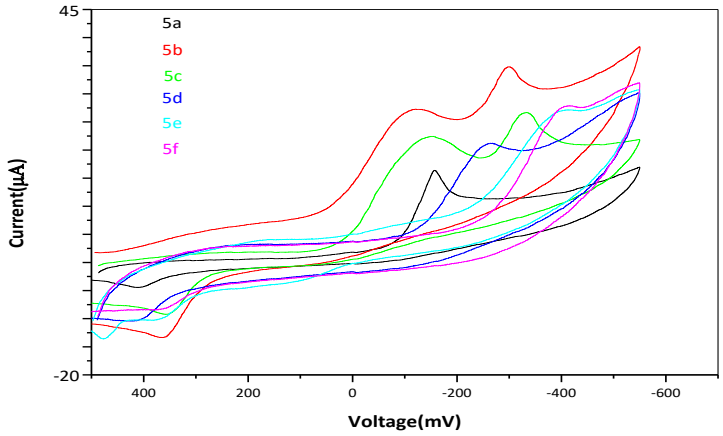


Fig.5: Cyclic voltammogram of 5(a-f) mV/s scan

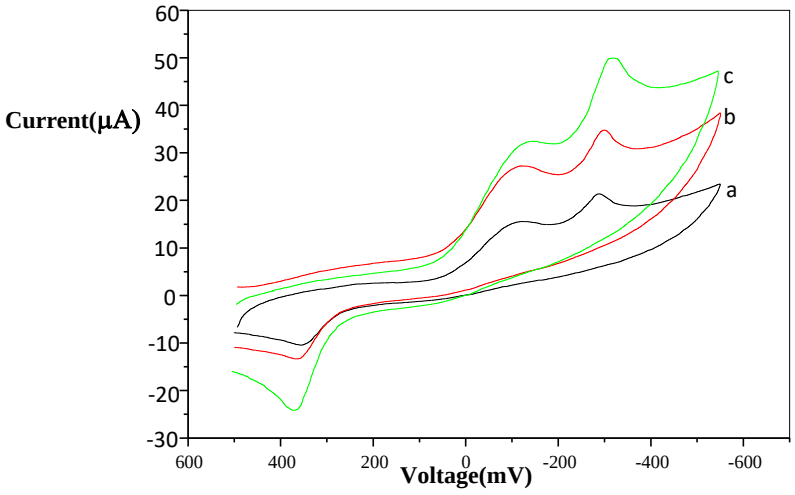


Fig. 6. Cyclic Voltammogram of 5bin different scan rate (a-25, b-50, c-75)

5. Antimicrobial screening:

5.1 Antibacterial study

The dye compounds are allowed for antibacterial studies and were evaluated by cup-plate method with different bacterial strains like. Escherichia coli, Bacillus subtilis, Pseudomonas aeruginosa, and staphylococcus aureus by using nutrient agar (NA) medium A.

DMSO is used for the preparation of test solutions with a concentration of 100µg/ml. The microorganisms were maintained in slant as solid culture. The solid slants were prepared by inoculating from the mother stock culture and finally the liquid media was subculture by inoculated from the solid

slants. The slants were allowed to incubate at 37 ^{0}C for 24 h. McCartney bottle having 20 ml of liquid nutrient agar media was sterilized in autoclave for about 15 min at 121 ^{0}C for 15 psi.

The disinfected media was dispensed into sterilised petri plates in aseptic condition in a laminar air flow. The uniform layers of media were made and allow it for solidification, followed by injecting the bacterial strains in to the petri plates. The spore suspension concentration was approximately 1.0×10^7 CFU/ml. To determine the antibacterial potency, the petri plates were made into three quarters and to each quarter a well was made in the media with the help of a sterilized cork borer (9 mm). The acknowledged concentrations of the standard drug amoxicillin and the test compounds were added to the labelled wells respectively. Thus, applied plates were allowed for incubation at 37 ^{0}C for about 24 h [38-40].

5.2 Antifungal study

The target compounds they did not showed significant antifungal activity

Table 7: Effect of scan rates on the reduction of ring at glassy carbon electrode

Compound	*E. coli*	*P.aeruginosa*	*B. subtilis*
5a	11.33±0.49	8.83±0.56	10.67±0.39
5b	10.17±0.24	8.33±0.38	8.67±0.43
5c	8.17±0.27	11.33±0.43	11.50±0.35
5d	11.33±0.49	8.83±0.56	10.67±0.39
5e	13.00±0.41	8.67±0.36	11.33±0.49
5f	16.50±0.36	11.67±0.38	11.33±0.60
Kenamycin	18.83±0.21	21.33±0.39	19.33±0.29

E. coli = Escherichia coli; P.aeruginosa =Pseudomonasaeruginosa; *B. subtilis*= Bacillus subtilis

Conflict of interest

The authors doesn't have any type of conflict of interest

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Supplementary materials

Supplementary data of the synthesized compounds are provided in a separate document.

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