

Synthesis, Characterization, Biological Activity, and Corrosion Inhibition Study of Two Dyes from 4-Aminophenol

Sura H. Kathim*

College of Science, Department of Chemistry, University of Waist, Kut, Iraq.
skathim@uowasit.edu.iq

Aseel F. Abdullah

College of Science, Department of Chemistry, University of Waist, Kut, Iraq.
aseelfarhan@uowasit.edu.iq

Mohammed M. Mohammed

College of Science, Department of Chemistry, University of Waist, Kut, Iraq.
sc.mohamad@gmail.com

Fatma A. Khazaal

College of Science, Department of Chemistry, University of Waist, Kut, Iraq.
fkhazal@uowasit.edu.iq

*Corresponding author: ; skathim@uowasit.edu.iq

Abstract-In the study, the reaction used to create the azo dyes (B and N) of 4-aminophenol with β -naphthol and 3-nitrophenol. These compounds were characterized by technology analysis as FT-IR and $^1\text{H-NMR}$ and physical properties were assessed. The synthesis compounds of biological activity were studied against two types of bacterial positive-grams (*Staphylococcus aureus*) and negative-grams (*E.coli*) and given good results. The azo compounds were studied as corrosion inhibitors in the dissolution of carbon steel 45 in (0. 1M) HCl solution. the inhibitors of dyes were inspected using the polarization technique. The compounds (B and N) show inhibition high efficiency.

Keywords: antibacterial; Azo; Corrosion; Carbon steel C45; Inhibitor; Polarization.

1. Introduction

Organic compounds with the general formula $\text{R}_1\text{-N=N-R}_2$, where R_1 and R_2 are alkyl or aryl groups, are classified as azo compounds. [1]. According to the paired azo chromophores, these compounds have been used in organic colorants. Group ($-\text{N}=\text{N}-$) that can be included in aromatic heterocyclic groups or analyzable aliphatic groups in addition to the benzene and naphthalene rings. These side groups are necessary to show the color of the dye [2] Changes in the extent to which electrons are not localized cause the color changes [3] Naphthalene compounds exhibit a diversity of biological activities including antimicrobial activities, [4] Azo compounds are widely recognized For its medicinal potential and antimicrobial applications [5, 6] Some studies have shown that corrosion inhibition by organic dyes is mainly attributed to the formation of complex compounds between metal ions and azo nitrogen. bound to the electrode surface (7,8). In this work, some azo dye derivatives were prepared as corrosion inhibitors. The work aims to prepare and evaluate the inhibitory properties of two compounds of azo dyes on the corrosion of carbon steel and to test the activity against two types of bacteria.

2.Experimental

2.1 Material and Reagents.

All of the compounds were obtained from Merck and utilized directly. At the Environmental Laboratory Center of the University of Baghdad, the samples were analyzed. Melting points were calculated using an uncorrected Gallen Kamp melting point equipment with open capillary tubes. The FTIR - 8400S spectra (KBr disc) were recorded with Shimadzu-2N in a College of Science, University of Baghdad, and $^1\text{H-NMR}$ spectra were recorded in University, Tehran, using a Bruker spectrometer model ultra-shield at (500MHz). DMSO- d_6 was utilized as a solvent while tetra methyl silane (TMS) served as an internal reference. The antimicrobial activity of synthesized compounds were evaluated at the University of Baghdad's Environmental Laboratory Center.

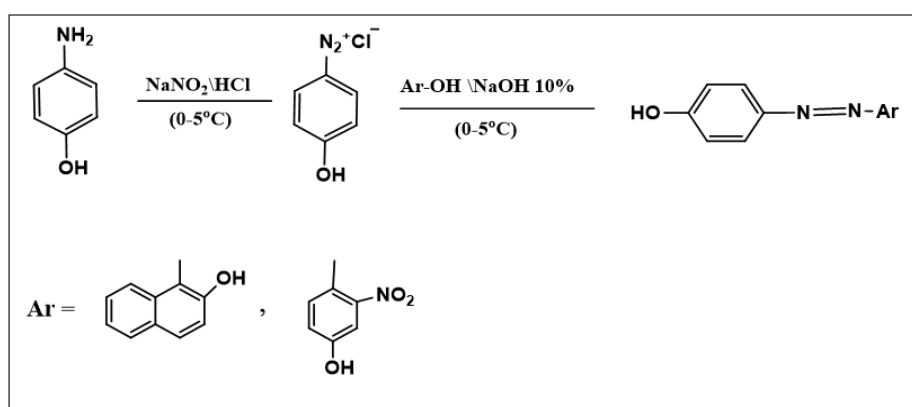
2.2 General procedure for the preparation of the compounds (B and N).

Preparation of Diazonium salt[4]

A-(0.0045 mol) of compound 4-aminophenol was dissolved in 5 ml of concentrated HCl and 5 ml of distilled water. The mixture was cooled in an ice bath until reaching 0-5 °C. Then a solution of NaNO_2 (0.0045 mol) in 2 ml of distilled water was prepared and added drop-by-drop to the reaction mixture with stirring for 10 min.

Coupling with phenols

B- A solution of appropriate phenols namely β - naphthol and 3-nitrophenol (0.0045 mol) in 5 ml of 10% NaOH was prepared and cooled in an ice bath then added carefully and very slowly with stirring to the prepared diazonium salt from the previous step . The reaction mixture was then left standing in the ice bath for 15 minutes until the crystallization is complete (giving a colored solid). The colored product was filtered, washed with cooled distilled **Scheme 1**.Table.2, the physical characteristics were given.



Scheme 1. Synthesis of compounds (β - naphthol and 3-nitrophenol).

2.3 Synthesis of inhibitors

0.05 g of previously prepared azo compounds(B and N) were dissolved in 3 mL of DMSO, then transferred into a 250 mL volumetric flask and the volume was supplemented to the mark with 0.1 M HCl.. The chemical composition of C45 typed in this study is shown in table.1.

Metal	C%	Si%	Mn%	S%	P%	Cu%	Ni%	Cr%	Fe%
Carbon	0.36-	0.15-	1.00-	0.05	0.05	0.50	0.20	0.20	96.88-
Steel 45	0.42	0.30	1.40						97.49

Table 1: Chemical composition of carbon steel C45. **The chemical create of C45 carbon steel**

2.4 Corrosion Potential Measurement.

The potential-stat set up includes a host computer, thermostat, magnetic stirrer, potential stat, Galvano stat, and (Emst at 4s, Palm Sens, Holland) sensors. The Pyrex cell has a capacity of (250 ml) and is made up of interior and external bowls. Three electrodes make up the electrochemical corrosion cell. With platinum having a length of 10 cm as an auxiliary electrode and carbon steel as the working electrode used to calculate its potential in relation to the reference electrode, the reference electrode is a saturated calomel.(Hg/Hg₂Cl₂ sat .KCl). For the purpose of establishing steady state open circuit potential, the working electrode was submerged in the test solution for 15 minutes.(E_{ocp}), then electrochemical measurements were performed in a potential range of ($\pm$ 200) mV. All tests were carried out at 298K by using a cooling-heating circulating water bath [9,10]. The corrosion cell made of Pyrex with (250ml) capacity Consists of two vessels, Internal and external. Three electrodes and a thermostat were replaced in an internal vessel [12].

3. Results and Discussion

3.1 Characterization

Azo dyes (N and B) were prepared by coupling reactions of diazonium salt of 4-amino phenol with substituted phenols (4-nitro phenol and β -naphthol). The physical properties of compounds (N and B) are listed in Table (2).

Table 2. Physical properties of azo compounds (A and B)

No	Name compound	Color	Molecular weight (g/mol)	Molecular structure	Yield %	Melting point (°C)
B	β - naphthol	Dark violet	264.28	C ₁₆ H ₁₂ N ₂ O ₂	50%	102-100
N	3-nitrophenol	Brown red	259.22	C ₁₂ H ₉ N ₃ O ₄	72%	105-107

FT-IR-spectra of compounds (B and N) revealed the presence of medium to strong bands at 3350 and 3278 cm⁻¹, respectively which attributed to the stretching vibration of OH in phenol. The bands at 1496-1465) cm⁻¹ respectively, attributed to the azo (

N=N) group. disappearance of sharp medium band at 3340 and 3287 cm^{-1} respectively belong to the amino group NH_2 as in figure (2) and (3).[13]

Table 3 . FT-IR spectral data of compounds (N and B).

Compound.	$\nu(\text{OH})$ cm^{-1}	$\nu(\text{C-H})_{\text{ar.}}$ cm^{-1}	$\nu(\text{C}=\text{C})$ cm^{-1}	$\nu(\text{N}=\text{N})$ cm^{-1}	νNO_2 cm^{-1}
N	3350	3007	1600	1496	1527
B	3278	3051	1627	1456	-

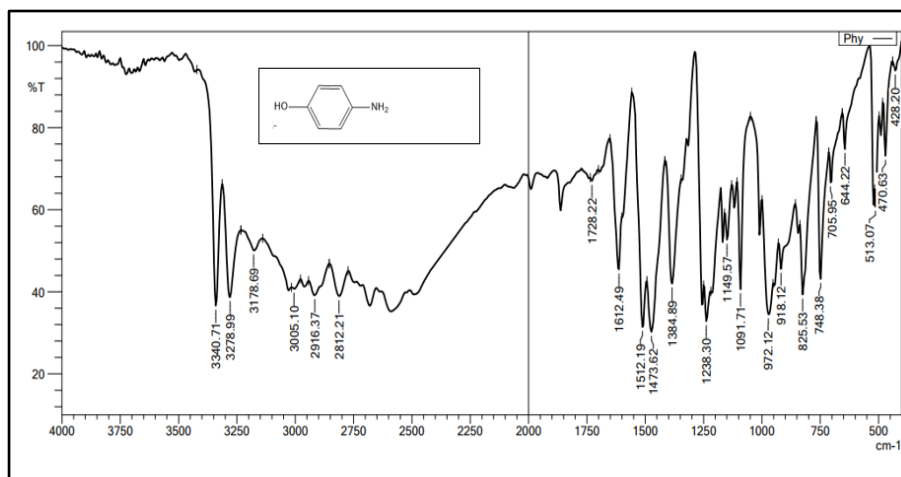


Fig.1. FT-IR spectra of compound [4-aminophenol]

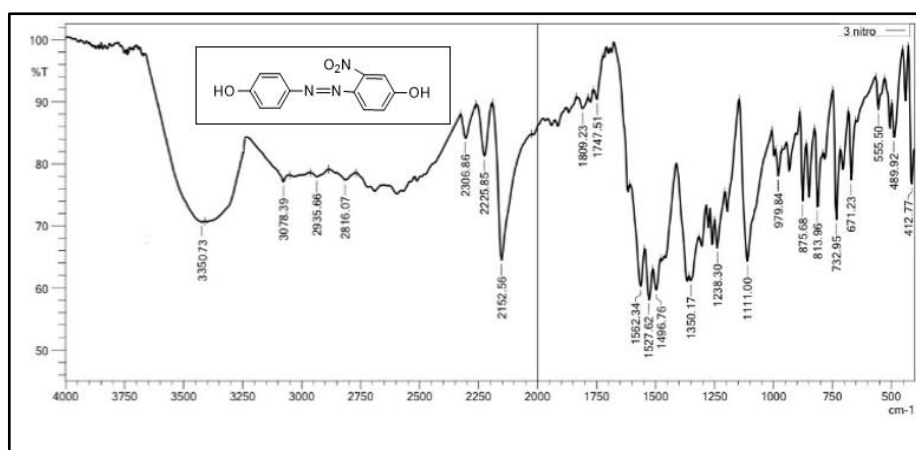


Fig .2. FT-IR spectra of compound (N).

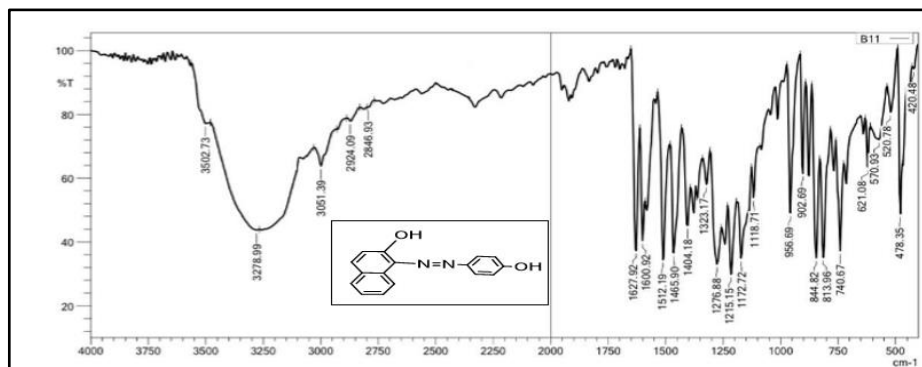


Fig.3. FT-IR spectra of compound(B).

$^1\text{H-NMR}$ spectra of compound (N) showed the following characteristic signals $\delta(\text{ppm})$: we find one signal 6.2 and signals multiple of 7.02-8.7

(m, 7H, Ar-H); 10.5 (s, 1H, OH) at in figure .4. $^1\text{H-NMR}$ spectra e find one signal 6.2 and multiplied of 7.02-8.7 of compound (B) showed the following characteristic signals $\delta(\text{ppm})$: 6.90-8.77(m,10H, Ar-H);9.98(s, 1H, OH), Figure .5. $^1\text{H-NMR}$ spectral of compounds (N and B) are listed in Table .4 [14].

Table 4. $^1\text{H-NMR}$ spectral data (ppm) of compounds N and B

No.	Compound structure	$^1\text{H-NMR}$ spectral data ($\delta(\text{ppm})$)
B		6.90-8.77(m,10H,Ar-H); 9.98(s,1H,OH)
N		6.20-8.15(m,7H,Ar-H) ;10.54(s,1H,OH)

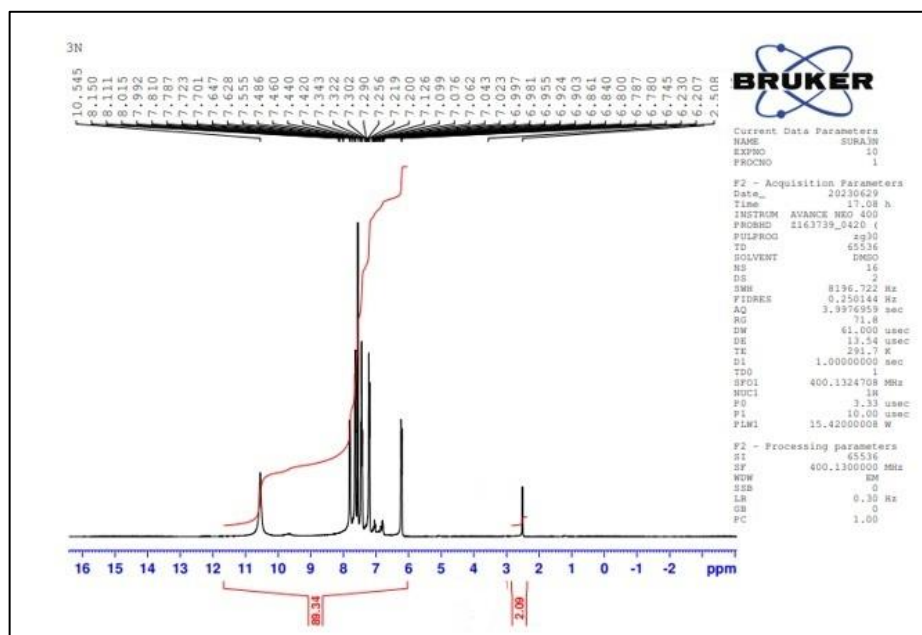
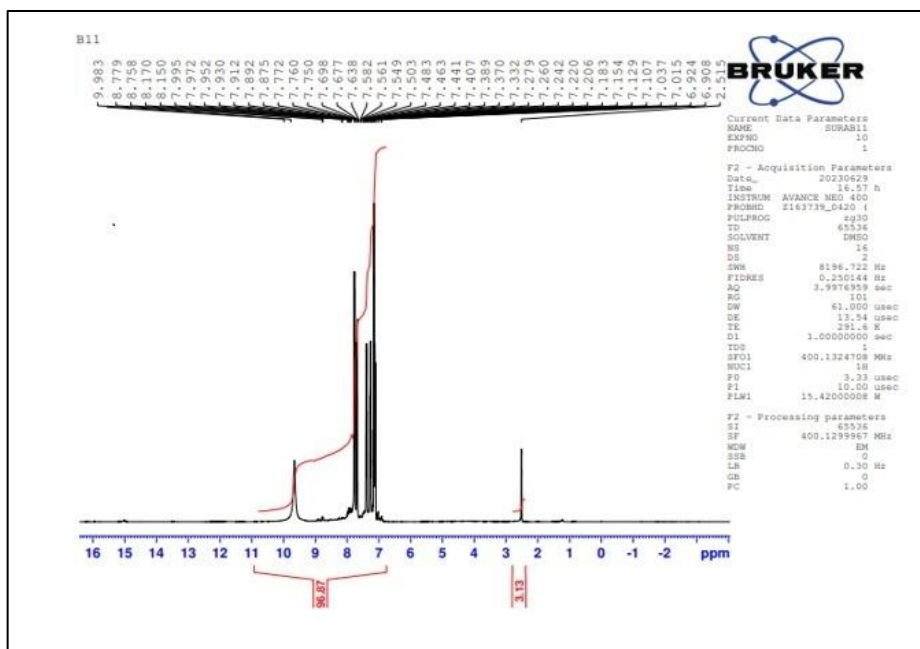


Fig.4. ¹H-NMR spectral (ppm) of compound(N).**Fig. 5.** ¹H-NMR spectral (ppm) of compound (B).

3.2 Polarization curves

The corrosion potential and corrosion current density (I_{corr})(E_{corr}) were extrapolated from the cathodic and anodic Tafel in the absence and presence of the inhibitor compounds in HCl (0.1M) solution. restructure, the anodic (ba) and cathodic (bc) Tafel slopes were determined (figure .3). illustrates the corrosion potential E_{corr} 's resulting data.(mV), corrosion current density i_{corr} (A/cm²), cathodic and anodic Tafel slopes (mV/Dec), and protection efficiency PE%

$$\%IE = \frac{(i_{corr})_o - (i_{corr})}{(i_{corr})_o} * 100 \quad (1)$$

When inhibitors are present, the corrosion current density is (i_{corr}), where (i_{corr}) is the corrosion current density in the absence of inhibitors [11,12]. The sample that was being examined was placed inside a corrosion cell, and the exposed surface's diameter to the solution was (16.55cm²). The entire system configuration for the polarization measurement is shown in Figure 6. The data shown in Table 4 as a consequence were used to evaluate the corrosion parameters. The effectiveness of additional chemical inhibition depends on many factors including the molecule's size, charge density, molecular structure, number of active absorption centers, and method of adsorption on the metal's surface. [5]

$$\%IE = \frac{(i_{corr})_o - (i_{corr})}{(i_{corr})_o} * 100 \quad (1)$$

Table 5. Corrosion parameters for blank and compounds (Band N) in HCl solutions.

No.	E corr.	I corr.	I corr./ r	Resis.	Anodic β	Cathodic β	Corr. rate, β	IE %
Blank	-0.527	163.5	3.269E-4	143.2	0.126	0.094	1.605	-

N	-0.618	23.99	798.E-5	1880	0.175	0.255	0.236	85
B	-0.637	16.33	266.E-5	2109	0.127	0.213	0.160	90

Notes: E corrosion, V; I corrosion, μA ; I corrosion per surface area, A/cm^2 ; Polarization Resistance, Ω ; Anodic β Tafel constant, V/decade; Cathodic β Tafel constant, V/decade; Corrosion rate, mm/year; IE% inhibition efficiency

The inhibition efficiency increases to (85% - 90%) with an increase Corrosion rate. depending on the concentration of the inhibitor, temperature and phenyl group.. This behavior might be explained by an increase in the number of molecules that have been adsorbed onto the metal surface.

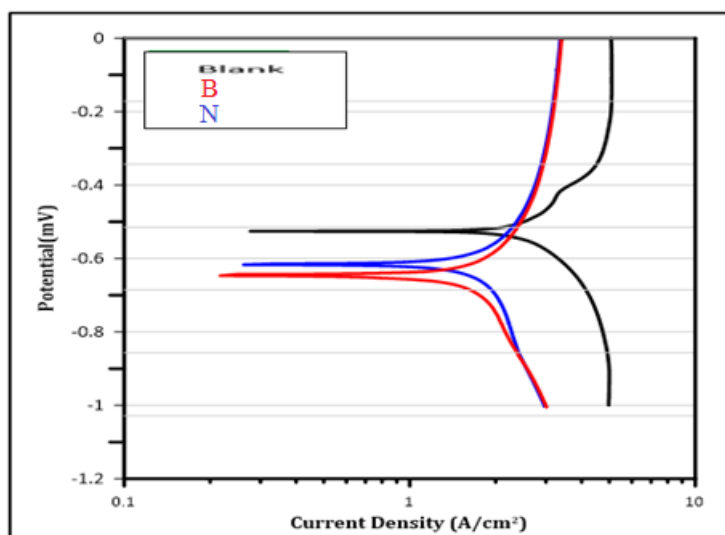


Fig . 6. Polarization curves for corrosion of blank HCl solution and N, and B.

3.3 Biological activity for compounds

Escherichia coli and *Staphylococcus aureus* were chosen as the tested bacteria for the biological activity of the novel compounds (B and N), which was investigated using the well diffusion method. It was used to investigate the efficiency of compounds against pathogenic bacteria under aerobic circumstances. [15]. both azo compounds B and N were given good inhibition of bacteria. table .6 shows the Growth inhibition of *E. coli* and *S. aureus* by using a good diffusion method. Figure 7. shows the images of dishes.

Table 6. Growth inhibition of *E. coli* and *S. aureus* by B and N by using well diffusion method.

No.	E.Coli	Staphylococcus aureus
B(226)	15	14
N(228)	12	11

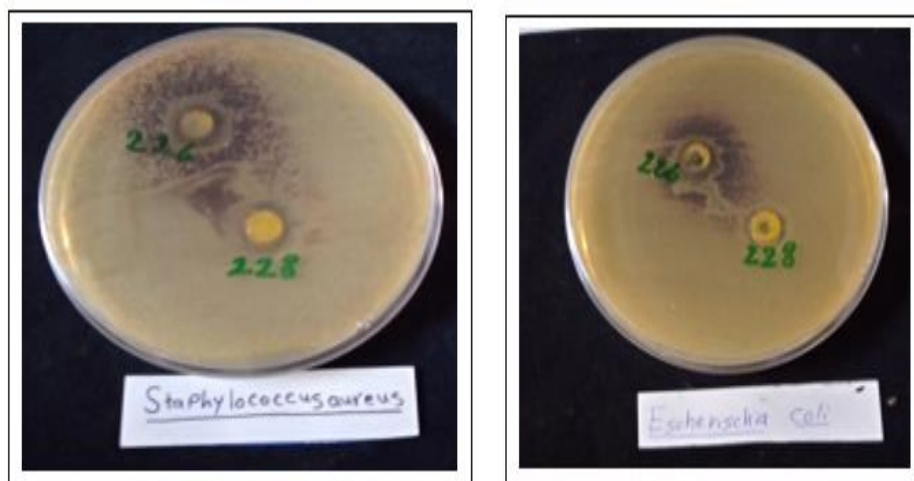


Fig.7. The inhibitory effects around each disc.

4-Conclusion

Azo compounds were prepared, synthesized and characterized by measuring IR, Hnmr, and their composition was proven. They were applied as a corrosion inhibitor and an antibacterial agent for two types of positive and negative bacteria. Organic substances that contain hetero-atoms (O, N) are among the efficient inhibitors of Steel-C 45. They were used to measure the loss by weight to evaluate the action of the inhibitor and its efficiency in inhibiting the corrosion - The efficiency was found to (90% - 85%) depending on the concentration of the inhibitor, temperature and phenyl group. The results of biological activity showed that compound B was more effective in inhibiting bacteria compared to compound N.

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