Bull. Chem. Soc. Ethiop. **2024**, 38(2), 473-479.
DOI: https://dx.doi.org/10.4314/bcse.v38i2.14

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

SYNTHESIS OF NEW AZO COMPOUNDS BASED ON 4-AMINOSALICYLIC ACID AND STUDY ANTI-CORROSIVE ACTIVITY

Nour Abd Alrazzak*

Department of Chemistry, College of Science for Women, University of Babylon, Babylon, Hilla, Iraq

(Received October 9, 2023; Revised December 8, 2023; Accepted December 10, 2023)

ABSTRACT. New azo dyes were prepared from 4-amino-2-hydroxy-benzoic acid in two steps; the first step includes preparation the diazonium salt. Then, diazonium compound coupled with different aromatic compounds containing donating groups (orcinol, 2,6-dimethylphenol, hydroquinone, catechol, 1,2,4-triazole, 2-methyl-naphthol and 4-toluidine, respectively). The physical properties of synthesized compounds were studied like melting point and solubility. The target molecules were characterized using FTIR, NMR and CHNS techniques. The activity of the compounds **1**, **3** and **5** as anticorrosion on carbon steel in 0.5 M HCl solution was studied using weight loss method at different times and two concentrations (0.003 M, 0.005 M) of inhibitors at 298 K. Compound **5** showed more inhibition efficiency and less weight loss at different concentration in comparison with compound **1** and compound **3**.

KEY WORDS: Azo dye, 4-Aminosalicylic acid, Diazonium salt, Anti-corrosion

INTRODUCTION

Azo dyes are widely used in industry and are considered to be one of the most important chromophores. Researchers have investigated straightforward synthesis methods for azo dyes and derivatives with a numerous application [1, 2]. Azo chromophores are a class of colorant organic substances that exhibit bright color in the visible spectrum and are used as tissue colorants and analytical chemical indicators. The existence of azo groups (-N=N-) in the skeletal structure sets them apart [3-6].

Azo dyes have been employed in a variety of fields, such as molecular identification, light-controlled polymers, inkjet printing, thermal transfer printing, photography, color additives, and liquid crystal design. In addition, they are used as colorants in more than 50% of all commercial dyes [7]. They are typically identified by their effective double bond between two atoms of nitrogen (-N=N-), which has several benefits for the textile industry [8]. In this sense, heterocyclic chemicals containing nitrogen, oxygen, or sulfur are necessary for azo dyes in order to increase the color of the dye and produce various hues with various intensities.

Nowadays, azo dyes integrating heterocyclic moieties outperform dyes made from aromatic amine regarding better solvatochromic behavior, tinctorial strength, thermal stability, and coloring properties [9-11].

Due to the existence of the -N=N- azo group, the majority of azo dyes are already colorful. The aromatic azo groups are also highly colored and frequently employed as dyes [12, 13]. Most of these substances are employed in the production of synthetic dyes, but several of them have also been noted to have intriguing applications in a number of fields, including corrosion inhibitors, medicines, and cosmetics [14-16]. Designing molecules with the structural characteristics of organic corrosion inhibitors that are easily and powerfully adsorbed on metal surfaces is made possible by the presence of nitrogen atoms in the azo linkage [17].

The aim of this work is the synthesis and characterization of new azo derivatives containing nitrogen and oxygen atoms, which are interesting in the field of corrosion.

---

*Corresponding author. E-mail: wsc.noorabd@uobabylon.edu.iq

EXPRIMENTAL

Materials

Merck and BDH Companies provided all chemicals. The following methods were employed in this research: The ^{1}H-NMR and ^{13}C-NMR data were analyzed using Bruker's (AC 400) NMR spectrometer (400 MHz), Shimadzu's (FT-IR 8400Series Japan), and other equipment.

Synthesis methods [18, 19]

At a temperature of 0–5 °C, 5 mL of HCl and 10 mL of distilled water were used to dissolve (0.01 mol, 1.53 g) of *p*-amino-*o*-hydroxy-benzoic acid. Sodium nitrite (0.01 mol, 0.67 g) was dissolved in distilled water (10 mL) and added to the first solution dropwise for 15 min. This mixture was added dropwise to solution of (1 g) NaOH in 15 mL of distilled water, and [0.01 mol, 1.24 g, 1.44 g, 1.01 g, 1.11 g, 1.01 g, 1.58 g, and 1.07 g] separately of orcinol, 2,6-dimethylphenol, hydroquinone, catechol, 1,2,4-triazole, 2-methyl-naphthol, and 4-toluidine, respectively. The precipitate was filtered, and washed three times with distilled water.

*Compound **1***. $C_{14}H_{12}N_2O_5$, color: yellow, yield: 92%, melting point = 227-230 °C; FT-IR (*v*, cm^{-1}): 3186 (O-H), 3068 (C-H$_{\text{Ar.}}$), 2902 (C-H$_{\text{Aliph.}}$), 1662 (C=O$_{\text{carboxyl}}$), 1618 (C=C), 1506 (N=N). ^{1}H NMR DMSO-*d*$_6$ (δ, ppm): 2.40 (H, C-H$_{\text{alph.}}$), 6.06 -7.47 (H, C-H$_{\text{arm.}}$), 7.83 (H, OH)$_{\text{phenol}}$, 11.02 (H, OH)$_{\text{carboxyl}}$. ^{13}C-NMR (δ, ppm): 18.20 (C, CH$_3$)$_{\text{alph}}$, 101.78-166.10 (C=C)$_{\text{arm.}}$, 160.12 (C, C-OH), 171.96 (C, C=O). CHNS found: C, 57.78; H, 4.46; N, 9.90; calculated: C, 58.33; H, 4.20; N, 9.72.

*Compound **2***. $C_{15}H_{14}N_2O_4$, color: orange, yield: 94%, melting point = 216-218 °C; FT-IR (*v*, cm^{-1}): 3101 (O-H), 3036 (C-H$_{\text{Ar.}}$, 2985 (C-H$_{\text{aliph.}}$), 1664 (C=O$_{\text{carboxylic acid}}$), 1597 (C=C), 1525 (N=N). ^{1}H NMR DMSO-*d*$_6$ (δ, ppm): 2.119 (H, C-H$_{\text{alph.}}$), 6.2-7.8 (H, C-H$_{\text{arm.}}$), 8.2 (H, OH)$_{\text{phenol}}$, 9.2 (H, OH)$_{\text{carboxyl.}}$ ^{13}C-NMR (δ, ppm): 17.24 (C, CH$_3$)$_{\text{alph.}}$, 108.73-162.26 (C=C)$_{\text{Ar.}}$, 163.96 (C, C-OH), 171.93 (C, C=O). CHNS found: C, 63.43; H, 5.27; N, 9.93; calculated: C, 62.93; H, 4.93; N, 9.79.

*Compound **3***. $C_{13}H_{10}N_2O_5$, color: red, yield: 89%, melting point = 209-211 °C; FT-IR (*v*, cm^{-1}): 3198 (O-H), 3088 (C-H$_{\text{Ar.}}$), 1662 (C=O$_{\text{carboxyl}}$), 1653 (C=C), 1558 (N=N). ^{1}H NMR DMSO-d$_6$ (δ, ppm): 6.9-8.1 (H, C-HAr.), 10.1 (H, OH)$_{\text{phenol}}$, 11.5 (H, OH)$_{\text{carboxyl.}}$ ^{13}C-NMR (δ, ppm): 102.19-139.16 (C=C)$_{\text{arm.}}$, 162.31 (C, C-OH), 172.34 (C, C=O). CHNS found: C, 57.52; H, 3.98; N, 10.53; calculated: C, 56.94; H, 3.68; N, 10.22.

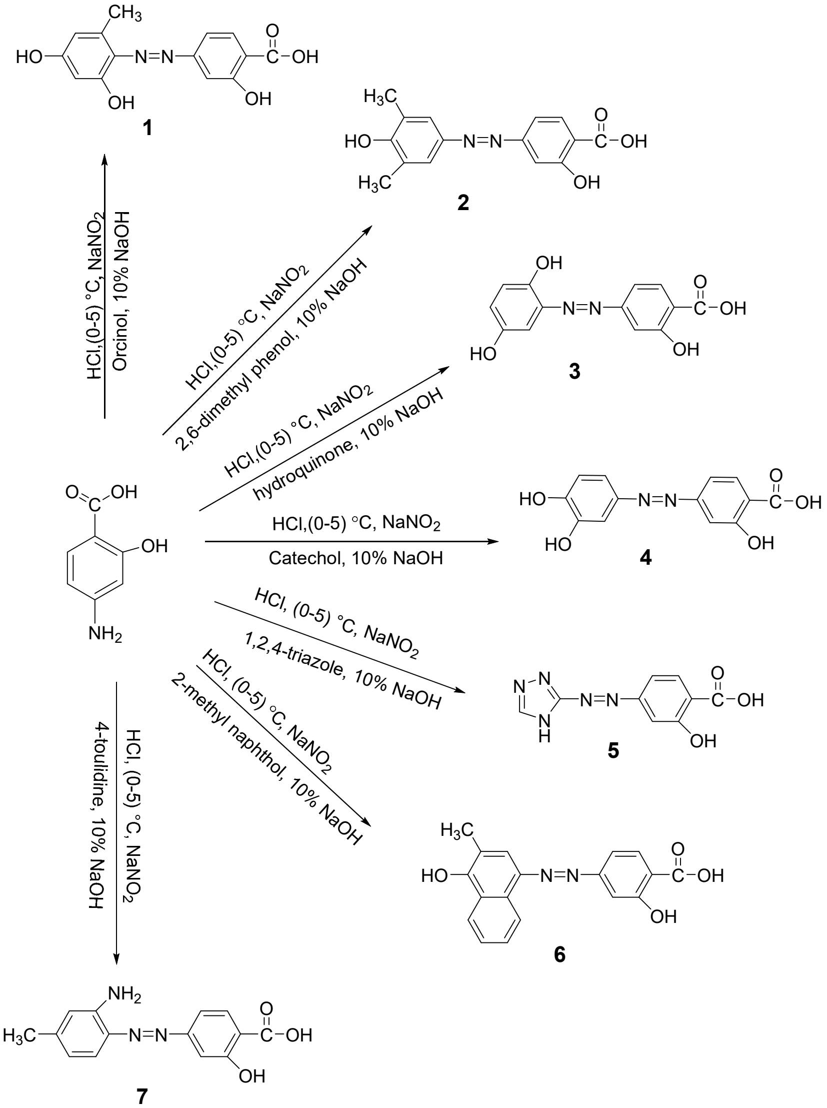
*Compound **4***. $C_{13}H_{10}N_2O_5$, color: orange, yield: 90%, melting point = 218-220 °C FT-IR (*v*, cm^{-1}): 3221 (O-H), 3059 (C-H$_{\text{Ar.}}$), 1662 (C=$_{\text{Ocarboxyl}}$), 1616 (C=C), 1508 (N=N). ^{1}H NMR DMSO-d$_6$ (δ, ppm): 6.2-8.2 (H, C-HAr.), 8.1 (H, OH)$_{\text{phenol}}$, 8.2 (H, OH)$_{\text{carboxyl}}$. ^{13}C-NMR (δ, ppm): 100.66-172.11 (C=C)$_{\text{Ar.}}$, 162.31 (C, C-OH), 172.34 (C, C=O). CHNS found: C, 57.44; H, 3.92; N, 10.67; calculated: C, 56.94; H, 3.68; N, 10.22.

*Compound **5***. $C_9H_7N_5O_3$, color: orange, yield: 90%, melting point = 238-240 °C; FT-IR (*v*, cm^{-1}): 3400 (O-H), 3300 (N-H), 3063 (C-H$_{\text{Ar.}}$), 1662 (C=O$_{\text{carboxylic}}$), 1616 (C=C), 1558 (N=N). ^{1}H NMR DMSO-*d*$_6$ (δ, ppm): 6.1-7.8 (H, C-H$_{\text{arm.}}$), 8.4 (H, OH)$_{\text{phenol}}$, 11.5 (H, OH)$_{\text{carboxyl.}}$ ^{13}C-NMR (δ, ppm): 100.69-166.82 (C=C)$_{\text{arm.}}$, 166.82 (C, C-OH), 172.39 (C, C=O). CHNS found: C, 46.81; H, 3.48; N, 30.33; calculated: C, 46.36; H, 3.03; N, 30.03.

*Compound **6***. $C_{18}H_{14}N_2O_4$, color: brown, yield: 91%, melting point = 212-214 °C; FT-IR (*v*, cm^{-1}): 3240 (O-H), 3049 (C-H$_{\text{Ar.}}$), 2874 (C-H$_{\text{Aliph.}}$), 1660 (C=O$_{\text{carboxylic}}$), 1622 (C=C), 1597 (N=N). ^{1}H NMR DMSO-*d*$_6$ (δ, ppm): 2.59 (H, C-H$_{\text{alph.}}$), 6.63-7.82 (H, C-H$_{\text{arm.}}$), 9.01 (H, OH)$_{\text{phenol}}$, 9.04

(H, OH)$_{\text{carboxyl}}$. ^{13}C-NMR (δ, ppm): 18.20 (C, CH_3)$_{\text{alph.}}$, 109.91-161.15 (C=C)$_{\text{Ar.}}$, 152.41 (C, C-OH), 162.33 (C, C=O). CHNS found: C, 67.59; H, 4.50; N, 8.89; calculated: C, 67.08; H, 4.38; N, 8.69.

Compound 7. $C_{14}H_{12}N_2O_3$, color: black, yield: 86%, melting point = 229-231 °C; FT-IR (*ν*, cm^{-1}): 3225 (O-H), 3076 (C-H$_{\text{Ar.}}$), 2956 (C-H$_{\text{alph.}}$), 1654 (C=O$_{\text{carboxylic acid}}$), 1616 (C=C), 1558 (N=N). ^{1}H NMR DMSO-d_6 (δ, ppm): 2.05 (H, C-H$_{\text{alph.}}$), 6.097-8.983 (H, C-H$_{\text{arm.}}$), 9.389 (H, OH)$_{\text{phenol}}$, 9.657 (H, OH)$_{\text{carboxyl}}$. CHNS found: C, 62.53; H, 5.21; N, 15.62; calculated: C, 61.99; H, 4.83; N, 15.49.



Scheme 1. Synthesis of compounds **1**-**7**.

Anticorrosion inhibitor

Steel specimens with dimensions of 2.5 cm × 4 cm × 0.5 cm were immersed in 0.5 M HCl in a beaker with and without addition of different concentrations (0.003 M, 0.005 M) of inhibitor compounds **1**, **2** and **3** for (1-6) h at 25 °C.

RESULTS AND DISCUSSION

4-Amino-2-hydroxy-benzoic acid which act as an electrophilic reagent, where reacted at 0 °C with electron-rich coupling compounds (orcinol, 2,6-dimethylphenol, hydroquinone, catechol, 1,2,4-triazole, 2-methyl-naphthol, and 4-toluidine) to form the azo compounds **1**–**7**.

*Compound **1***. FTIR shows the disappearance of NH_2 at (3495, 3387) cm^{-1} and the occurrence of N=N at (1506) cm^{-1}. ^{1}H NMR spectrum show an occurrence signal at 2.012 for $(C\text{-}H)_{aliph.}$, at 6.120-7.893 for (H, $C\text{-}H_{Ar}$), at 9.389 for (OH) phenol, and at 11.021 for $(OH)_{carboxylic}$. ^{13}C-NMR spectrum show an appearance signal at 171.96 for (C, C=O) carboxylic, (C, CH_3) at 18.20 and at (101.78-166.10) for ($C\text{-}CH_{Ar}$).

*Compound **2***. FTIR show disappearance of NH_2 at (3495, 3387) cm^{-1} and occurrence N=N at (1525) cm^{-1}. ^{1}H NMR spectra show occurrence signal at 2.119 for $(C\text{-}H)_{aliph.}$, at 6.2-7.8 for (H, C-H $_{Ar}$) and at 9.2 for $(OH)_{carboxylic}$, 8.2 for $(OH)_{phenol}$. ^{13}C-NMR spectra show an appearance signal at 171.93 for (C, C=O) $_{carboxylic}$, (C, CH_3) at 17.24 and at (108.73-162.26) for ($C{=}C_{Ar.}$).

*Compound **3***. FTIR shows the disappearance of NH_2 at (3495, 3387) cm^{-1} and the occurrence N=N at (1558) cm^{-1}. ^{1}H NMR spectrum show appearance signals at 6.9-8.1 for (H, $C\text{-}H_{Ar.}$) and at 11.5 for $(OH)_{carboxylic}$, 10.1 for $(OH)_{phenol}$. ^{13}C-NMR spectrum show the occurrence signal at 172.34 for (C, $C{=}O)_{carboxylic}$, and at (102.19-139.16) for $(C{=}C)_{Ar.}$.

*Compound **4***. FTIR shows the disappearance of NH_2 at (3495, 3387) cm^{-1} and the occurrence of N=N at (1508) cm^{-1}. ^{1}H NMR spectrum show occurrence signals at 6.2-8.2 for (H, C-H $_{Ar}$) and at 8.2 for $(OH)_{carboxylic}$, 8.1 for $(OH)_{phenol}$. ^{13}C-NMR spectra show an occurrence signal at 172.34 for (C, C=O) $_{carboxylic}$, and at (100.66-172.11) for the $(C{=}C)_{Ar}$.

*Compound **5***. FTIR shows the disappearance of NH_2 at (3495, 3387) cm^{-1} and the occurrence of N=N at (1504) cm^{-1}. ^{1}H NMR spectrum show occurrence signals from 6.1-7.8 for (H, C-H $_{Ar}$) and at 11.5 for $(OH)_{carboxylic}$, 8.14 for $(OH)_{phenol}$. ^{13}C-NMR spectrum show an appearance signal at 172.39 for (C, $C{=}O)_{carboxylic}$, and at (100.69-166.82) for the $(C{=}C)_{Ar}$.

*Compound **6***. FTIR shows the disappearance of NH_2 at (3495, 3387) cm^{-1} and the occurrence of N=N at (1597) cm^{-1}. ^{1}H NMR spectrum show appearance signals at 2.59 for (H, CH_3), from 6.63-7.82 for (H, $C\text{-}H_{Ar}$) and at 9.04 for $(OH)_{carboxylic}$, 9.01 for $(OH)_{phenol}$. ^{13}C-NMR spectrum show an occurrence signal at 162.33 for (C, $C{=}O)_{carboxylic}$, (C, CH_3) at 18.20 and at (109.91-161.15) for $(C{=}C)_{Ar}$.

*Compound **7***. FTIR shows the disappearance of NH_2 at (3495, 3387) cm^{-1} and the occurrence of N=N at (1558) cm^{-1}. ^{1}H NMR spectrum show occurrence signals at 6.097-8.983 for (H, C-H $_{Ar}$), at 9.389 for (H, OH) and 9.657 for (H, $OH)_{carboxylic}$.

Synthesized compounds shown in Table 1 are soluble in solvents like absolute ethanol, acetone and dimethylsulfoxide, and insoluble in solvents like hexane and water.

Table 1. Solubility of synthesis compounds **1**-**7**.

Comp. No.	Solvents				
	EtOH	Acetone	Hexane	DMSO	Water
1	+	+	-	+	-
2	+	+	-	+	-
3	+	+	-	+	-
4	+	+	-	+	-
5	+	+	-	+	-
6	+	+	-	+	-
7	+	+	-	+	-

Table 2. Weight loss and inhibition efficiency IE% of carbon steel corrosion in 0.5 M HCl at 289 K.

Immersion time										
Concentration	1 hour		2 hours		3 hours		4 hours		5 hours	
	Weight loss	Inhibition efficiency IE%	Weight loss	Inhibition efficiency IE%	Weight loss	Inhibition efficiency IE%	Weight loss	Inhibition efficiency IE%	Weight loss	Inhibition efficiency IE%
1 M HCl	0.1050	-	0.1311	-	0.1720	-	0.193	-	0.245	-
1										
$3 * 10^{-3}$	0.0351	66.5	0.0390	62.8	0.0423	62.7	0.0479	54.3	0.0495	52.8
$5 * 10^{-3}$	0.0237	77.4	0.0253	75.9	0.0277	73.6	0.0294	72	0.0312	70.2
3										
$3 * 10^{-3}$	0.0290	72.3	0.0321	69.4	0.0342	67.4	0.0361	65.6	0.0377	64.1
$5 * 10^{-3}$	0.0171	83.7	0.0194	81.5	0.0275	73.8	0.0301	71.3	0.0332	68.3
5										
$3 * 10^{-3}$	0.0220	79	0.0251	76.1	0.0273	74	0.0302	71.2	0.0321	69.4
$5 * 10^{-3}$	0.0151	85.6	0.0169	83.9	0.0188	82.2	0.0221	78.9	0.0249	76.2

Anti-corrosion study proven that azo compounds **1**, **3** and **5** act as inhibitors via make a bond through adsorption on the surface of carbon steel and make barrier layer between the steel and corrosive substance in Figures 1-6. The highest inhibition efficiency at maximum concentration of 1×10^{-3} M of inhibitor at 298 K, and with increases of immersion time from one to five hours using

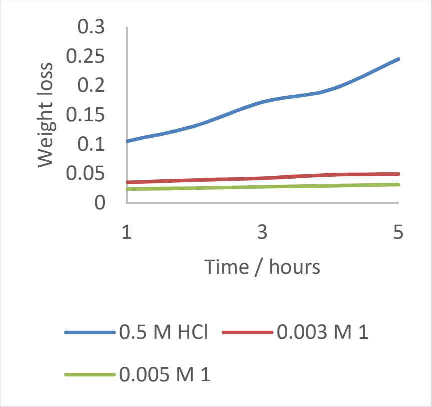


Figure 1. Weight loss of **1** against immersion time at 298 K.

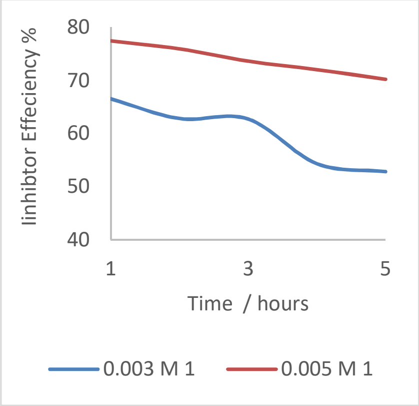


Figure 2. Inhibitor efficiency of **1** against immersion time at 298 K.

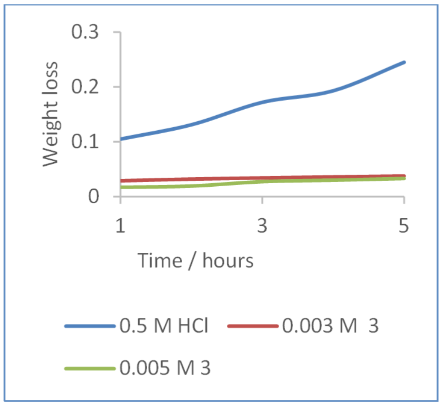


Figure 3. Weight loss of **3** against immersion time at 298 K.

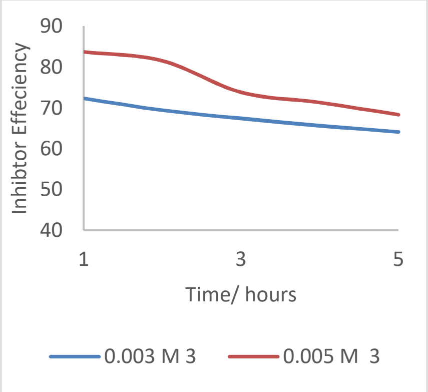


Figure 4. Inhibitor efficiency of **3** against immersion time at 298 K.

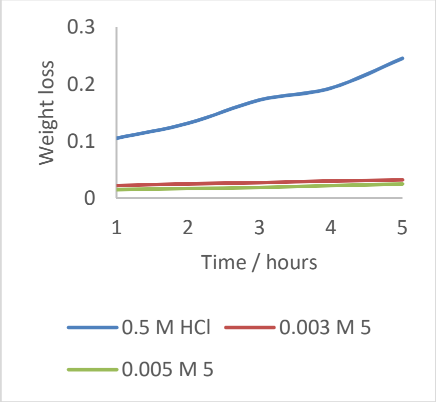


Figure 5. Weight loss of **5** against immersion time at 298 K.

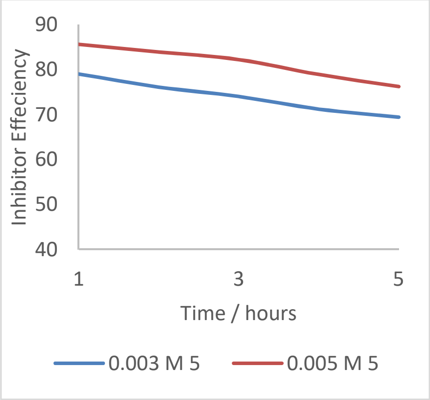


Figure 6. Inhibitor efficiency of **5** against immersion time at 298 K.

two concentration (0.003 M, 0.005 M) of inhibitors at same temperature 298 K, the inhibition efficiency decrease. Compound **5** show more inhibition efficiency and less weight loss at both concentration in comparison with compound **1** and compound **3**. Compound **5** structure that contain heterocyclic moiety (triazole), appeared the adsorption on carbon steel via lone pair of electron on nitrogen atom as well as pi electron of aromatic ring.

CONCLUSION

Series of new azo compounds were prepared from reaction of 4-amino-2-hydroxy-benzoic acid with different coupling compounds containing electron-donating groups with good yield. By using the weight loss method for the synthesized surfactant **1**, **3** and **5**, the inhibition efficiency was found to increases with increasing the concentration of prepared azo compounds (inhibitors) and decrease with time at 298 K in an acidic medium.

REFERENCES

1. Tahir, T.; Ashfaq, M.; Saleem, M.; Rafiq, M.; Shahzad, M.I.; Mojzych M.; Kotwica-Mojzych, K. Pyridine scaffolds, phenols and derivatives of azo moiety: Current therapeutic perspectives. *Molecules* **2021**, 26, 4872.
2. Sahilu, R.; Eswaramoorthy, R.; Mulugeta, E.; Dekebo, A. Synthesis, DFT analysis, dyeing potential and evaluation of antibacterial activities of azo dye derivatives combined with in silico molecular docking and ADMET predictions. *J. Mol. Struct.* **2022**, 1265, 133279.
3. Snigur, D.V.; Chebotarev, A.N.; Bevziuk, K.V. Acid-base properties of azo dyes in solution studied using spectrophotometry and colorimetry. *J. Appl. Spectrosc.* **2018**, 85, 21-26.
4. Darwish, E.S.; Mosselhi, M.A.; Altalbawy, F.M.; Saad, H.A. Synthesis, acidity constants and tautomeric structure of the diazonium coupling products of 2-(benzylsulfanyl)-7H-purin-6-one in its ground and excited states. *Molecules* **2011**, 16, 8788-8802.
5. Mohammed, H.S.; Tripathi, V.D. Medicinal applications of coordination complexes. *J. Physics: Conference Series* **2020**, 1664.
6. Mohammed, H.S.; Tripathi, V.D.; Darghouth, A.A.; Mothhar T. Synthesis, characterization, DFT calculation and antimicrobial activity of Co(II) and Cu(II) complexes with azo dye. *J. Physics: Conference Series* **2019**, 1294.
7. Gurses, A.; Açıkyıldız, M.; Gurnes, K.; Gurses, M.S. *Classification of Dye and Pigments. Dyes and Pigments*, Springer International Publishing: Online Publication; **2016**; pp. 31-45.
8. Benkhaya, S.; Mrabet, S.; El Harfi, A. Classifications, properties, recent synthesis and applications of azodyes. *Heliyon* **2020**, 6, e03271.
9. Ravi, B.N.; Keshavayya, J.; Kumar, V.; Kandgal, S. Synthesis, characterization and pharmacological evaluation of 2-aminothiazole incorporated azo dyes. *J. Mol. Struct.* **2020**, 1204, 127493.
10. Nagaraja, O.; Bodke, Y.D.; Pushpavathi, I.; Kumar, S.R. Synthesis, characterization and biological investigations of potentially bioactive heterocyclic compounds containing 4-hydroxy coumarin. *Heliyon* **2020**, 6, e04245.
11. Manjunatha, B.; Bodke, Y.D.; Jain, R.S.K.; Lohit, T.N.; Sridhar, M.A. Novel isoxazolone based azo dyes: synthesis, characterization, computational solvatochromic UV-Vis absorption and biological studies. *J. Mol. Struct.* **2021**, 1244, 130933.
12. Bhagat, S.D.; Thakare, N.S. Synthesis and spectral analysis of some new phenolic azo compounds. *Int. J. ChemTech Res.* **2017**, 10, 160-163.
13. Asad, S.; Amoozegar, M.A.; Pourbabaee, A.A.; Sarbolouki, M.N.; Dastgheib, S.M.M. Decolouration of textile azo dyes by newly isolated halophilic and halotolerant bacteria. *Bioresour. Technol.* **2007**, 98, 2082-2088.
14. Clofent, D.; De Homdedeu, M.; Munõz-Esquerre, M.; Cruz, M.J.; Munõz, X. Sudan red dye: A new agent causing type-2 occupational asthma. *Allergy Asthma Clin. Immunol.* **2020**, 16, 7.
15. Vázquez-Ortega, F.; Lagunes, I.; Trigos, Á. Cosmetic dyes as potential photosensitizers of singlet oxygen generation. *Dyes Pigment*. **2020**, 176, 108248.
16. Madkour, L.H. ; Kaya, S.; Guo, L.; Kaya, C. Quantum chemical calculations, mol.cular dynamic (MD) simulations and experimental studies of using some azo dyes as corrosion inhibitors for iron. Part 2: Bis–azo dye derivatives, *J. Mol. Struct.* **2018**, 1163, 397–417.
17. Fouda, A.S.; Mukhtar, M.M. New arylazodyes as corrosion inhibitors for mild steel in HCl solution. *Chem. Eng. Commun.* **2011**, 198, 1111-1128.
18. Nour, A.A.; Suad, T.S.; Hazim, Y.A.; Mohanad, M.K.; Mawahib, M.A. Photocatalytic degradation efficiency of azo dye in aqueous phase using different photo. *Bull. Chem. Soc. Ethiop.* **2020**, 34, 463-469.
19. Hasan, S.M.; Hussein, A.A.; Zahira, C.; Zahia, Z.; Hussein, N.A. Synthesis characterization, DFT calculation and biological evaluation of azo dye ligand containing 1,3-dimethyxanthine and its Co(II), Cu(II) and Zn(II) complexes. *Bull. Chem. Soc. Ethiop.* **2023**, 37, 347-356.