

Corrosion control of Cu–Ni alloy in hydrochloric acid by amines compounds

A.A. Mahmmod, M.H. Ismael, A.A. Fadhil and N.H. Kurshed

University of Diyala, College of Engineering, Chemical Department, Diyala University,
Baquba City 32001, Daiyla Governorate, Iraq

*E-mail: alnuimiadiba@yahoo.com

Abstract

Inhibitors of corrosion are chemicals materials that, when added in little amount to an environment impede the development of corrosion reactions. The inhibitors use is represent one of selections of protecting alloys of metals from corrosion, which leads to protect surfaces of metal in corrosive environments. Most organic compounds inhibitors that contain nitrogen, are effective inhibitors in the acidic medium, especially hydrochloric acid. Copper represents noble metal and requiring very strong oxidants for its dissolution or corrosion. The electrolytic plating and chemical dissolution are the main processes used in the electronic devices fabrication. Alloys made of copper are widely used in chemical processes especially when heat and electrical conductivity are important factors in these processes, there is very wide range of copper metal using in commercial applications. The corrosion inhibition or corrosion control of alloy made of copper (Cu) – nickel (Ni) in hydrochloric acid (6% HCl) at the range of temperature of (40–60°C) was studied in the absence and presence of the inhibitors used in the experimental work were ethylenediamine (EDA) and tetraethylenepentamine (TEPA) at the range of concentration of (1–10 g/l). The technique of weight loss was used to evaluate the data of corrosion rate. EDA & TEPA were used as organic inhibitors of corrosion. Corrosion rate decreased with increases of inhibitor concentration, while it increased with increases of temperature. The adsorption isotherm of both inhibitors on metal surface used in this research was found to follow Freundlich. The kinetic-thermodynamic data and adsorption isotherms were used to evaluate the values of equilibrium constants (K).

Key words: *corrosion, copper–nickel alloy, corrosive solution, amines compounds inhibitor.*

Received: March 3, 2019. Published: April 26, 2019

doi: [10.17675/2305-6894-2019-8-2-15](https://doi.org/10.17675/2305-6894-2019-8-2-15)

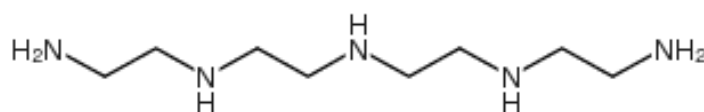
1. Introduction

Processes of corrosion are responsible for numerous losses mainly in the industrial field, the best way to fight corrosion growth, among the different methods to shun loss or extirpation of metal exterior, the use of inhibitor is represent one of the best methods known of corrosion protection and one of the most useful on the industrial field. This method is following stand up due to low cost and practice method [1–11]. Metallic copper is a very widely used material due to for excellent electrical and thermal conductivities.

Many of industrial equipment are constructed from copper, such as cooling tower parts, heat exchangers tubes, *etc.*, which maybe in contact with different aqueous – oxygen containing environments. Oxygen presence may lead to corrosion problems and searching for control of corrosion solutions is one of interesting research fields. Commonly, the metallic materials corrosion in acidic media causes significant costs [12]. Corrosion can be controlled using different techniques; one of these is inhibitors of corrosion [13–17]. Generally organic inhibitors have hetero atoms (oxygen, nitrogen, and sulphur). Hetero atoms have higher electron density and basicity, thus work as effective inhibitor of corrosion, as well as hetero atoms (O, N, and S) are the active centers for the process of adsorption on the surface of metal. The most inhibitors are organic adsorbed on the surface of metal by displacing molecules of water on the surface and forming a compact barrier are showed by the existing data, non-bonded availability (lone pair) and p-electrons in molecules of inhibitor facilitate transfer of electron from the inhibitor to the metal, a coordinate covalent bond involving on the transfer of electrons to the surface of metal from inhibitor may be formed, the chemisorption bond strength depends upon the electron density on the donor atom of the functional group and the group polarizability [18]. The inhibition mechanism of the anticorrosion compounds used in present paper is ascribed to their interactions with the surface of metal by surface adsorption. The adsorption of an inhibitor on a surface of metal depends on the nature and the surface charge of the metal, the mechanism adsorption, chemical structure of inhibitor, and the type of the corrosive solution [19–21]. The aim of the present paper was to study the effect of temperature and concentration of inhibitor on the corrosion of alloy made of (copper–nickel) in the corrosive solution in the presence of ethylenediamine (EDA) and tetraethylenepentamine (TEPA) as corrosion inhibitors. The chemical structures of both inhibitors are shown below:



TEPA



EDA

2. Experimental work

The alloy of copper–nickel corrosion was studied by using technique of weight loss in absence and presence inhibitors (1, 4, 7, and 10 g/l) as a concentrations of corrosion inhibitors in corrosive solution (6% HCl) at different temperature (40, 50, and 60°C). The alloy used in this research is a square shape specimen with dimensions of (2×2×0.1) cm

and analysis of Cu–Ni alloy as following: Sn = 0.1479%, Fe = 0.2%, Zn = 0.137%, Sb = 0.5%, Ni = 9.98%, Si = 0.02%, S = 0.0168%, Al = 0.0149% and Cu = 88.993%.

The samples alloy made of copper–nickel alloy were immersed in 100 cm³ acidic solution contained in a conical flask, they were exposed for a period of 24 hours at a concentration of inhibitor and temperature were used in this experiments. Weight losses were determined in absence and presence of EDA & TEPA, in the present work the corrosion rate units were g/m²·day (gmd).

3. Results and discussion

3.1 Measurements of weight loss represent by corrosion rates

The rates of corrosion of Cu–Ni alloy in corrosive solution represented by (6% HCl) as a temperature function in absence and presence of different concentrations of inhibitor are listed in Table 1 using technique of weight loss. The values of rates of corrosion were calculated using the following equation:

$$CR = (W_1 - W_2) / A \cdot t \quad (1)$$

Where CR is corrosion rate (gmd), W_1 and W_2 (g) are the mass before and after immersion, A is the surface area of Cu–Ni alloy samples (m²), and t is time of experiment (day). While values of inhibitors efficiency were determined using the following equation:

$$\%IE = \frac{C_R^0 - C_R}{C_R^0} \times 100 \quad (2)$$

Table 1. Temperature effect and concentration of inhibitor on the corrosion of alloy made of (Cu–Ni) in corrosive solution (6% HCl).

Inhibitor type	Concentration of inhibitor (g/l)	Temp. (°C)	Corr. rate (gmd)	Efficiency (%)
Nil	0	40	12.3	–
		50	15.26	–
		60	20.47	–
EDA	1	40	9.31	24.3
	4		7.06	42.6
	7		4.89	60.2
	10		2.82	77
	1		50	11.93
	4		9.17	39.9

Inhibitor type	Concentration of inhibitor (g/l)	Temp. (°C)	Corr. rate (gmd)	Efficiency (%)
TEPA	7	60	6.20	59.4
	10		4.32	71.7
	1	60	17.06	16.7
	4		12.95	36.7
	7		10.14	50.5
	10		7.33	64.2
	1	40	10.21	17
	4		8.09	34.2
	7		7.20	41.5
	10		5.38	56.3
	1	50	12.7	16.8
	4		10.056	34.10
7	9.07		40.6	
10	6.75		55.8	
1	60	17.17	16.12	
4		13.516	33.97	
7		12.282	40.0	
10		9.536	53.41	

Table 1 and Figures 1, 2 show the variation of the rate of corrosion with concentration of inhibitor at different values of temperature. The addition of inhibitors reduces the rate of corrosion, this reduction depend on the inhibitors type. Figure 3 represents the comparison between EDA & TEPA at different temperatures, the rate of corrosion increases with temperature increasing. Figure 4 represent the relationship between efficiency and inhibitor concentration. The efficiency of inhibitor used in present work increases with concentration increasing from these figures (EDA) is the best.

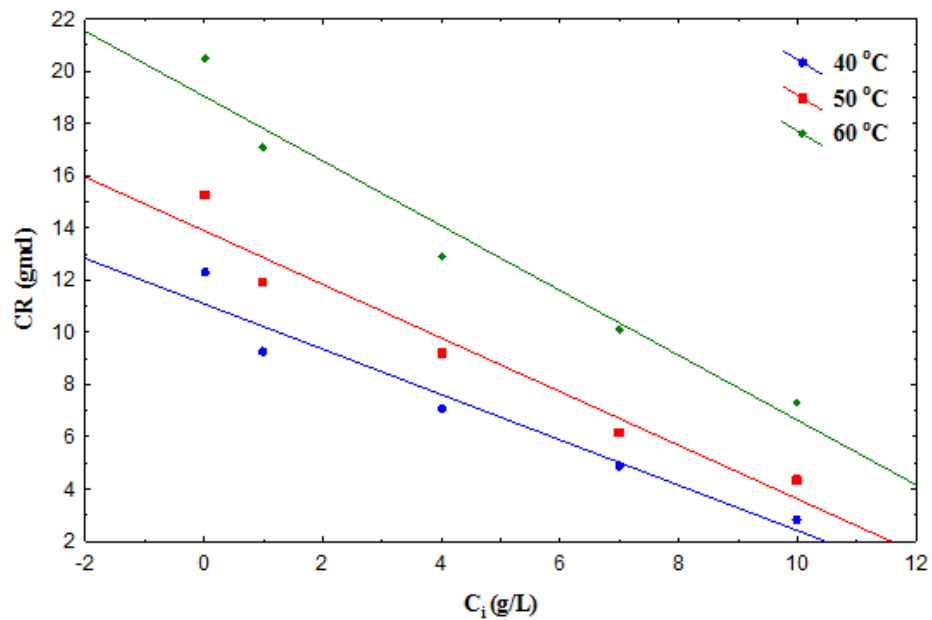


Figure 1. Effect of the concentration of EDA on the corrosion rate of Cu–Ni alloy in hydrochloric acid at different temperatures.

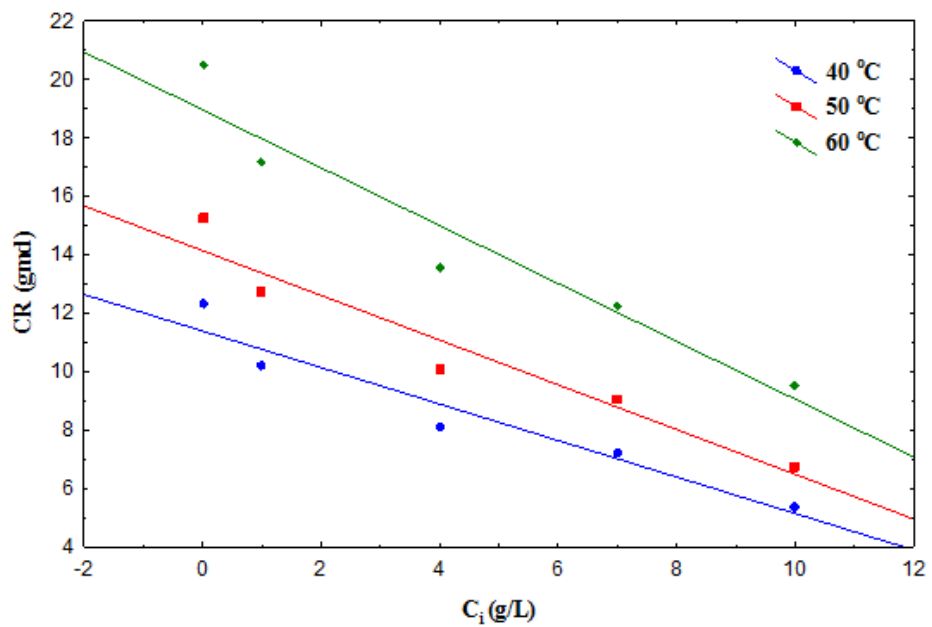


Figure 2. Effect of the concentration of TEPA on the corrosion rate of Cu–Ni alloy in hydrochloric acid at different temperatures.

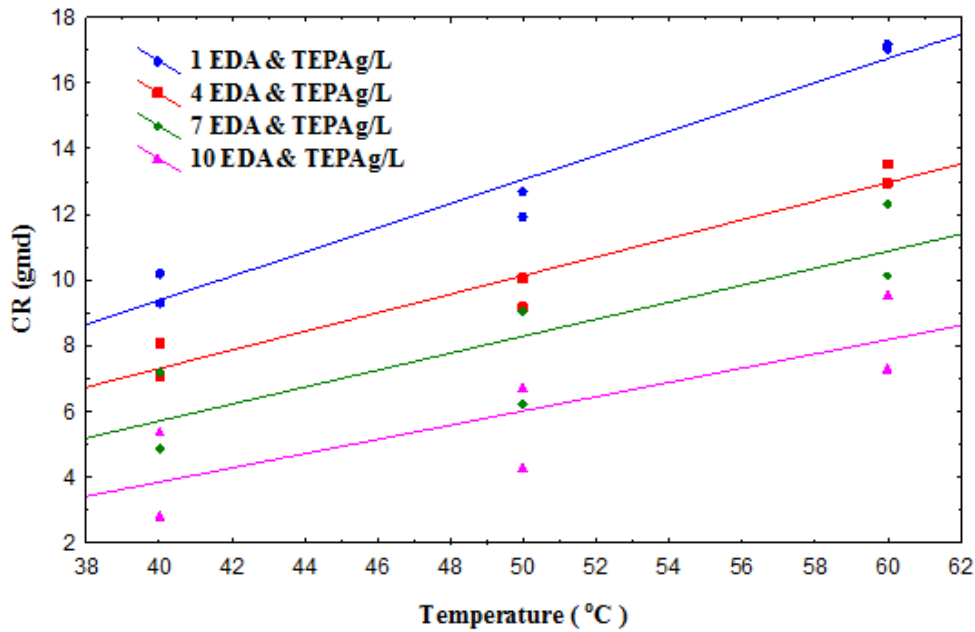


Figure 3. Effect of temperature on the corrosion rate of Cu–Ni alloy in hydrochloric acid in presence of comparison between EDA and TEPA.

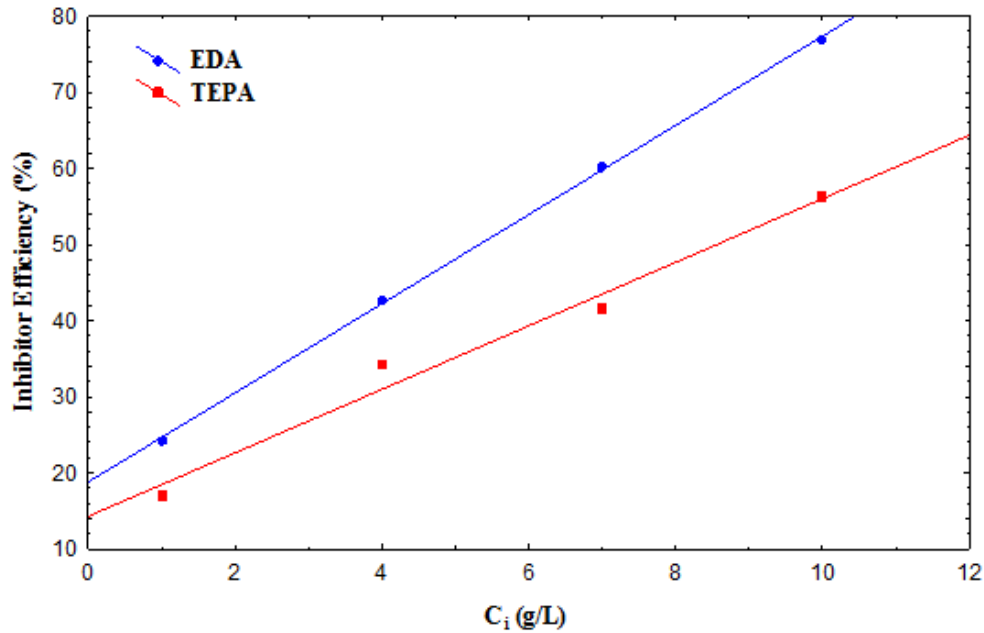


Figure 4. Efficiency of inhibitors (EDA and TEPA) vs. concentration of inhibitors at 40°C.

3.2 Effect of temperature and parameters of thermodynamic

In an acidic solutions (hydrogen evolution), the corrosion rate increases exponentially with temperature [22]. Activation parameters for some systems can be estimated either from an Arrhenius equation (Eq. 3) [23].

$$C_R = A \exp(-E_a / RT) \tag{3}$$

The surface coverage (θ) data are very useful while studying the mechanism of adsorption. When the surface fraction covered is evaluated as a function of the inhibitor concentration at constant temperature, adsorption isotherm could be estimated at equilibrium condition. In present study three adsorption isotherms were used. Langmuir adsorption isotherm (Eq. 4), Freundlich adsorption isotherm (Eq. 5), and kinetics – thermodynamics isotherm (Eq. 6).

$$C/\theta = 1/K_L + C \quad (4)$$

$$\ln\theta = \ln K_F + n \ln C \quad (5)$$

$$\ln(\theta/(1-\theta)) = \ln K' + y \ln C \quad (6)$$

K_L and K_F are the equilibrium constants of Langmuir adsorption isotherm and Freundlich adsorption isotherm. While n is a power constant in Freundlich adsorption isotherm. In Eq. 6, K' is a constant, and y is the number of molecules of inhibitor occupying one active site. Equilibrium constant corresponding to adsorption isotherm is given by $k = k'^{1/y}$. Values of $y > 1$ implies the inhibitor multilayer formation on the metal surface. Values of $y < 1$ mean a given inhibitor molecules will occupy more than one active site. Equations 4–6 can be represented graphically as shown in Figures 5, 6, 7, 8, 9 and 10 for Langmuir, Freundlich adsorption, and kinetics – thermodynamics isotherms respectively. Table 2 collects the adsorption parameters for all mentioned adsorption isotherms that obtained from graphical representations. [24].

Table 2. Adsorption parameters of EDA and TEPA.

Inhibitor	T (°C)	Langmuir isotherm		Freundlich isotherm		Kinetics isotherm		
		K_L (L/ml)	ΔG_{ads}^0 (KJ/mol)	K_F (L/ml)	n''	C_i (g/l)	$\ln A$	E_a (kJ/mol)
EDA	40	4.2431	-14.215	0.234641	2.03915	0	2.399	51.14528
	50	4.6119	-14.893	0.211887	1.93535	1	2.512	60.78373
						4	2.492	60.93072
	60	5.7751	-15.976	0.165564	1.72205	7	2.638	72.97691
10						2.833	95.99433	
TEPA	40	5.5671	-14.921	0.168908	2.00320	1	2.397	52.18664
						4	2.366	51.53623
	50	5.6239	-15.425	0.167027	2.00481	7	2.388	53.64165
						10	2.418	57.41901

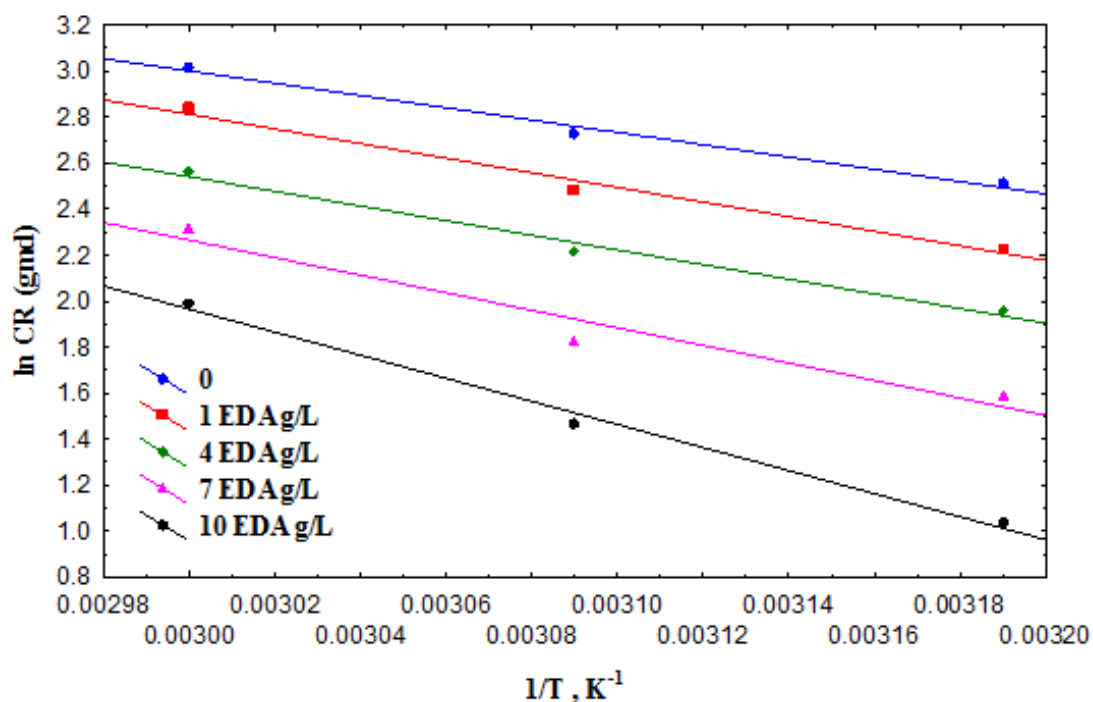


Figure 5. Arrhenius plot of Cu–Ni alloy in hydrochloric acid containing various concentrations of EDA that affect the corrosion rate at different temperatures (40–60°C).

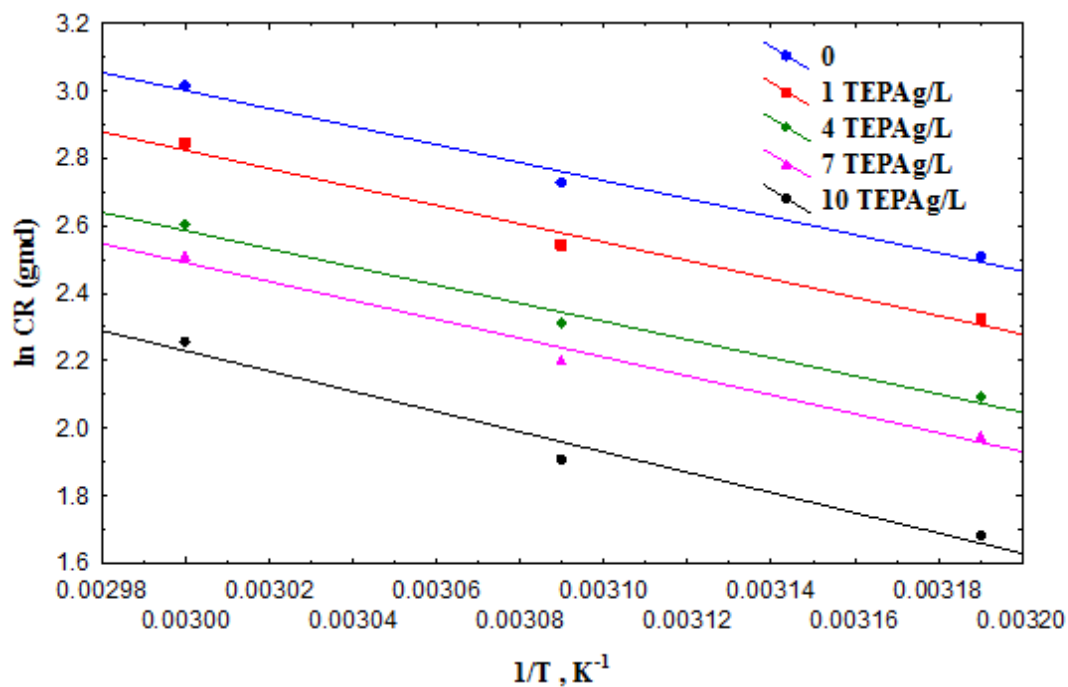


Figure 6. Arrhenius plot of Cu–Ni alloy in hydrochloric acid containing various concentration of TEPA that affect the corrosion rate at different temperatures (40–60°C).

4. Conclusion

The ethylenediamine (EDA) acts as good and efficient inhibitor better than tetraethylenepentamine (TEPA) for the corrosion of Cu–Ni alloy in 6% hydrochloric acid medium. Efficiency of inhibition increases with inhibitor concentration increasing and decreases with increasing of temperature, maximum inhibition efficiency for EDA and TEPA were found to be 77% & 56.3% at the higher inhibitor concentration of 10 g/l and temperature at 40°C. The adsorption on the surface of metal (Cu–Ni alloy) of inhibitors used in this research followed Freundlich adsorption isotherm. Inhibitors containing nitrogen, oxygen, sulphur and phosphorous in the conjugated system have particularly been reported as efficient inhibitors of corrosion. These compounds can adsorb on the surface of metal blocking the active sites and thereby decreasing the rate of corrosion.

References

1. M.S. Al-Otaibi, A.M. Al-Mayouf, M. Khan, A.A. Mousa, S.A. Al-Mazroae and H.Z. Alkathlan, Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media, *Arabian J. Chem.*, 2012, 1–7.
2. I.B. Obot, N.O. Obi-Egbedi and S.A. Umoren, Antifungal drugs as corrosion inhibitors for aluminium in 0.1 M HCl, *Corros. Sci.*, 2009, **51**, no. 8, 1868–1875.
3. M. Mihit, S. El Issami, M. Bouklah, L. Bazzi, B. Hammouti, E. Ait Addi and R. Salghi, The inhibited effect of some tetrazolic compounds towards the corrosion of brass in nitric acid solution, *Appl. Surf. Sci.*, 2006, **252**, no. 6, 2389–2395.
4. S. El Issami, L. Bazzi, M. Mihit, B. Hammouti, S. Kertit, E. Ait Addi and R. Salghi, Triazolic compounds as corrosion inhibitors for copper in hydrochloric acid, *Pigm. Resin Technol.*, 2007, **36**, no. 3, 161–168.
5. A.A. Khadom, A.S. Yaro and A.A.H. Kadhum, Adsorption mechanism of benzotriazole for corrosion inhibition of copper-nickel alloy in hydrochloric acid, *J. Chil. Chem. Soc.*, 2010, **55**, no. 1, 150–152.
6. E.M. Sherif and Su-M. Park, Inhibition of copper corrosion in 3.0% NaCl solution by N-phenyl-1,4-phenylenediamine, *J. Electrochem. Soc.*, 2005, **152**, no. 10, B428–B433.
7. A. Yildirim and M. Cetin, Synthesis and evaluation of new long alkyl side chain acetamide, isoxazolidine and isoxazoline derivatives as corrosion inhibitors, *Corros. Sci.*, 2008, **50**, no. 1, 155–165.
8. J.R.B. Thavamani, E. Rani and T. Jeyaraj, Inhibition of the corrosion of aluminium in alkaline medium by 1-(phenyl)-3-(2-hydroxy phenyl)-propenone in the presence of tetrabutylammonium bromide, *Chem. Sin.*, 2012, **0**, no. 6, 1358–1368.
9. A.A. Mahmmod, I.A. Kazarinov, A.A. Khadom and H.B. Mahood, Experimental and theoretical studies of mild steel corrosion inhibition in phosphoric acid using tetrazoles derivatives, *J. Bio- and Tribo-Corrosion*, 2018, **4**, no. 4, 58.

10. K.F. Khaled, Adsorption and inhibitive properties of a new synthesized guanidine derivative on corrosion of copper in 0.5 M H₂SO₄, *Appl. Surf. Sci.*, 2008, **255**, 1811–1818.
11. A. Popova, M. Christov and A. Zwetanova, Effect of the molecular structure on the inhibitor properties of azoles on mild steel corrosion in 1 M hydrochloric acid, *Corros. Sci.*, 2007, **49**, no. 5, 2131–2143.
12. S.A. Umoren, I.B. Obot and I.O. Igwe, *Open Corros. J.*, 2009, **2**, 1–7.
13. A.Y. Musa, A.A. Kadhum, A.B. Mohamad, M.S. Takriff, A.R. Daud and S.K. Kamarudin, On the inhibition of mild steel corrosion by 4-amino-5-phenyl-4H-1,2,4-triazole-3-thiol, *Corros. Sci.*, 2010, **52**, no. 2, 526–533.
14. D.N. Komov, A.A. Mahmmod, A.A. Matikenova, L.A. Isaicheva, A.P. Kriven'ko and I.A. Kazarinov, Effect of Tetrazolic Corrosion Inhibitors on the Corrosion and Electrochemical Behavior of Steel in Phosphoric Acidic Solutions, *Izvestiya Sarat. unta. Novaya seriya. Biologiya. Khimiya. Ekologiya*, 2014, **14**, no. 2, 32–38 (in Russian).
15. E.M. Sherif and Su-M. Park, Effects of 2-amino-5-ethylthio-1,3,4-thiadiazole on copper corrosion as a corrosion inhibitor in aerated acidic pickling solutions, *Electrochim. Acta*, 2006, **51**, no. 28, 6556–6562.
16. A.A. Khadom, A.Y. Musa, A.H. Kadhum, A. Mohamad and M.S. Takriff, Adsorption kinetics of 4-amino-5-phenyl-4H-1,2,4-triazole-3-thiol on mild steel surface, *Port. Electrochim. Acta*, 2010, **28**, no. 4, 221–230.
17. T. Poornima, J. Nayak, A.N. Shetty, Effect of 4-(N,N-diethylamino) benzaldehyde thiosemicarbazone on the corrosion of aged 18 Ni 250 grade maraging steel in phosphoric acid solution, *Corros. Sci.*, 2011, **53.11**: 3688–3696.
18. U.R. Evans, *The Corrosion and Oxidation of Metals*, Hodder Arnold, 1976.
19. K.C. Emregül, R. Kurtaran and O. Atakol, An investigation of chloride-substituted Schiff bases as corrosion inhibitors for steel, *Corros. Sci.*, 2003, **45**, no. 12, 2803–2817.
20. A. Lalitha, S. Ramesh and S. Rajeswari, Surface protection of copper in acid medium by azoles and surfactants, *Electrochim. Acta*, 2005, **51**, no. 1, 47–55.
21. A.S. Fouda, M. Abdallah and M. El-Hoseiny, Acrylonitrile derivatives as corrosion inhibitors for Cu10Ni alloy in 0.5 M hydrochloric acid solution, *Afr. J. Pure Appl. Chem.*, 2013, **7**, no. 7, 252–263.
22. A.A. Khadom and A.S. Yaro, Protection of low carbon steel in phosphoric acid by potassium iodide, *Prot. Met. Phys. Chem. Surf.*, 2011, **47**, no. 5, 662.
23. A.S. Yaro, R.K. Wael and A.A. Khadom, Reaction kinetics of corrosion of mild steel in phosphoric acid, *J. Univ. Chem. Technol. Metall.*, 2010, **45**, no. 4, 443–448.
24. S.A. Umoren and E.E. Ebenso, The synergistic effect of polyacrylamide and iodide ions on the corrosion inhibition of mild steel in H₂SO₄, *Mater. Chem. Phys.*, 2007, **106**, no. 2–3, 387–393.

