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EXPERIMENTAL CORROSION CONTROL OF CUPRONICKEL ALLOYS IN ACIDIC MEDIUM BY COMPOUNDS OF AMINES

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ABSTRACT

Our research focused on the capability of Naphthylamine (NPHA) & Phenylenediamine (PHDA) to inhibit the corrosion of Cu-Ni alloys in HCl solution, which was examined using the weight wastage technique. Increasing the concentration of (NPHA & PHDA) reduced the corrosion values, demonstrating the influence of corrosion inhibition. Adsorption of (NPHA) on the surface of the (Cu-Ni) alloy plays an important role in repression activities. Corrosion inhibitors are compounds that, when introduced in tiny quantities to an acidic media, prevent the corrosion process from expanding. Inhibitors are one of the most effective methods of preventing corrosion in metal alloys, and they are widely utilized. Corrosion prevention of (Copper-Nickel) alloy in acidic solutions (3.5 % HCl) at the temperature (30 - 50 ℃) was calculated in two cases; with and without inhibitors. Naphthylamine (NPHA) and Phenylenediamine (PHDA) indicated that the substances used in the experiential work were at concentrations (2 - 8 g/l). The method of weight-loss was employed to assess the values of corrosion rates. Corrosion rate value decreased with an increase in the concentrations of inhibitor and decreasing the temperature. The values of adsorption isotherm of inhibitor (NPHA) on the sample surface were observed to conform to Freundlich, in another hand the data of kinetic-thermodynamic and isotherms of adsorption were applied to assess the equilibrium constants (K) values.

KEYWORDS

Organic Compounds inhibitor; kinetic-thermodynamic ; Adsorption Isotherms ; Copper – Nickel alloy; Corrosive medium.

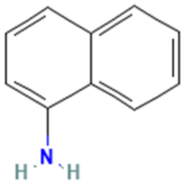
1. INTRODUCTION

Copper alloys are versatile and have been used in many industries due to their submersible conductivity. Even with its excellent properties, copper is susceptible to corrosion. Therefore, understanding why copper corrodes is important for both industries and individuals, because it can drive significant financial losses and safety concerns. Copper corrosion can appear in different forms, each with its characteristics and effects. The chemical industries use copper alloys widely in some important operation units such as fractionating columns, evaporators, condensers, etc. One considerable corrosion challenge is acidic corrosion, which comprises severe localized corrosion of steel pipelines due to connection with acidic fluids in industrial processes such as petroleum output and transportation. Copper is not attacked under normal conditions by hydrochloric acid; However, in the presence of oxidizing conditions, copper becomes vulnerable to attack by acids. It dissolves, for example, in hot sulfuric acid, and it also dissolves in nitric acid. Copper does not supplant hydrogen of the sour solution and it is thence inoffensive in non-oxidizing sour ambience. Nonetheless, the general acidic environment includes the dissolved air that allows some corrosion. Many organic compounds are used to prevent the corrosion of copper (Mahmmod et al., 2024; Khadom and Mahmmod, 2022; Mahmmod, A.A., 2019; Mahmmod et al., 2020; Al-Itawi et al., 2019; Semiletov, A.M., 2017; Rashid, W.T. 2024). Copper, thanks to its many attractive properties, has become a metal that has captured human attention. It is frequently utilized in the production of exchangers and connectors, as well as in the construction of water desalination facilities and drinking water distribution pipes. It can also endure the pressure of the atmosphere and chemicals. However, it is prone to corrosion. In more acidic conditions, this occurrence produces irreversible damage, which can degrade environmental quality, impact human health, and result in economic losses. Among them are synthetic and organic inhibitors, which are the most commonly used against copper corrosion in acidic environments. The adsorption at the mineral-solution interface represents the initial stride for organic inhibitors that operate in the necessary environment. The process of adsorption relies on the quality of the metal superficies, the operating temperature, the solution chemical composition and the electronic of the molecules. Adsorption requires an attractive force between the adsorbent and the metal. Adsorption: Whether it is Physisorption, chemisorption, or a combination of both, is determined depending on the type of forces. (Abed, R.H., 2024; Akkar and Alali, 2023; Mohammed, M., 2023;Mahmmod et al., 2019). Physisorption denotes electrostatic attractive forces between inhibiting the organic ions and the electrical shipments metal surface. Chemisorption denotes the combined work between non-participate electrons and the mineral to form and shape a coordination type of ligation.

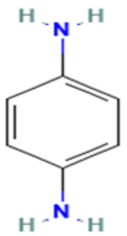
Heteroatoms possess high electron density, so they act as an efficient inhibitor of corrosion, as well as heteroatoms (O, S, P, N, and Se), which are the efficient pivots for the procedure of adsorption on the mineral exterior (Afia et al., 2014; Mahmmod et al., 2018; Atia and Saleh, 2003; Afia et al., 2013; Afia et al., 2012; Refaey et al., 2008; Anejjar et al., 2014).The almost discouragers organics are adsorbed on the mineral surface by supplanting water molecules on the surface. In addition formation of a built-in barricade is demonstrated by the existent data, non-bonded obtainability (lonesome pair) and p-electrons in the molecules of inhibitor expedite the convey of an electron to the mineral from the inhibitor, a coordinate covalent band encompassing on the relocate of electrons to the surface of mineral from inhibitor perhaps created, the chemisorption bond vigor relies on the electron intensity on the contributor atom of the workable group and the collection polarizability (Anejjar et al., 2015; Al-Otaibi et al., 2014; Obot et al., 2009). The mechanism of inhibition of the inhibitors applied in the current paper is imputed to their interactions together the surface of the metal by surface adsorption. The inhibitor adsorption onto a mineral surface counts on the metal surface shipment, the mode adsorption, corrosive milieus type and inhibitor chemical structure (El Issami et al., 2007; Sherif and Park, 2005; Khaled, K.F., 2008 ; Popova et al., 2007; Lalitha et al., 2005; Mahmmod et al., 2020). The current effort pursues to look at the temperature influence on the alloy's corrosion, in addition influence of inhibitor concentration, in the corrosive medium with NPHA & PHDA as corrosion inhibitors.

2. EXPERIMENTAL WORK

The chemical structure of joint inhibitors in experimental labor is shown beneath:



NPHA



PHDA

In this search, an effort was made to assess these inhibitors for copper-nickel (Cupronickel) in HCl acid. The weight loss method was used to study the corrosion behavior of copper-nickel alloy with and without inhibitors (2,4,6, and 8 g/l) as well as a concentration of corrosion inhibitors in the corrosive environment (3.5% HCl) at various temperatures (30,40, and 50°C). The alloy's dimensions are (2×2×0.1) cm. Cu-Ni alloy has the following chemical composition: Fe = 0.2%, Sn = 0.1479%, Sb = 0.50%, Zn = 0.137%, Ni = 9.98%, S = 0.0168%, Si = 0.02%, Al = 0.0149%, and Cu = 88.993%. The sample's surface was cleaned with sandpaper, washed with distilled water, and then rinsed with ethanol. Finally, the sample was dried using hot air. The alloy was covered in a 200 cm^3 corrosive solution in a conical carafe. The alloy left for 24 hours in a specific inhibitor and temperature. Weight loss was specified with and without (NPHA& PHDA). In the experiences, the corrosion rate unit was g/m^2•day (gmd).

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements illustrated by corrosion rates

The rates of corrosion of models (paradigms) in the corrosive milieu were clarified by (3.5% HCl) as a function of temperature, once without the inhibitors, and again using inhibitors at multiple concentrations which is registered in Table 1 utilizing the technique of weight lack or loss. The corrosion rate values are calculated by using the subsequent Eq.1:

$$CR = W_1 - W_2 / A \times t \qquad (1)$$

Where CR denotes corrosion rate (gmd), W1 and W2 (g) symbolize the mass prior to and after inundation, A signifies the surface part of samples (m^2), and t is a time of experimentation (day). whilst values inhibitors efficacy values werecalculated employing the next Eq.2:

$$\% IE = (C°_R - C_R / C°_R) \times 100 \qquad (2)$$

Table 1 and Fig.1, 2, 3, 4, and 5 depict the variation in corrosion rate and competence with amine compound inhibitor concentrations at various temperatures. The rate of corrosion decreases as the inhibitor concentration increases; this decrease is dependent on the amine compound's inhibitor type. The rate of corrosion rises with temperature elevating. Fig.6 illustrates the linkage between temperature and efficiency in addition to the corrosion rate. When the increases temperature value the corrosion rate increases while the process efficiency decreases with it. The leverage of increased temperature of the corrosive solution is immediately proportional to the copper corrosion rate, as the higher the temperature the rate of corrosion is in addition to what is mentioned above the effect of the increases of the temperature is inversely proportional to the process efficiency.

Table 1 shows that the mineral sample has been significantly corroded in the corrosion solution when there are no amine compounds inhibitors and at different temperatures recorded values of (11.86, 14.85 &19.35) g/m^2•day. This scenario changes when the contents of the inhibitor are added to the surface of copper. Table 1 also it can be shown that the corrosion rate was significantly reduced when inhibitors were present, indicating that those retarders have an effective ability to protect against the dissolution of alloy in the acid solution. It has also been spotted that the efficacy of inhibitors increases with increasing inhibitor concentration. In the NPHA experiment, the corrosion began to decrease gradually with increasing the concentration of NPHA, giving efficiencies up to 75.89 % at the concentration of 8 g/l and 30 ℃, although little concentration of this inhibitor, the efficiency value was good. At this point, the corrosion rate is at its lowest value (2.859(gmd)). Moreover, the same inhibitor scenario is repeated during the PHDA addition. The rapport between the efficiency ratio and the concentration of the organic inhibitor remains directly related, noting that the PHDA inhibitor gave a very small efficiency value, and this indicates that it is inefficient in protecting copper. Table 1 also shows that the corrosion rate was significantly reduced when the inhibitor (NPHA) was present, indicating its effective ability to protect against the decay of copper in the acid solution. It was also observed that the efficiency increases with increasing the concentration of the inhibitor, on the contrary, the type (PHDA) inhibitor has a limited ability to protect against corrosion, it is clear that (NPHA) is better from all figures.

Table 1 Influence of Temperature and Concentration of Inhibitors on the Specimen Corrosion which is made of (Cu-Ni) alloy in an acidic environment (3.5%HCl).

Inhibitor Form	Inhibitor Focus (g/l)	Temp. (℃)	Corr. Rate (gmd)	Efficiency (%)
Nil	0	30	11.86	/
		40	14.85	/
		50	19.35	/
NPHA	2	30	9.896	16.56
	4		6.460	45.53
	6		4.553	61.61
	8		2.859	75.89
	2	40	13.036	12.21
	4		10.265	30.87
	6		7.815	47.37
	8		5.652	61.94
	2	50	17.943	7.27
	4		15.105	21.93
	6		11.877	38.62
	8		9.464	51.09
PHDA				
	2	30	11.551	2.6
	4		10.56	10.96
	6		8.628	27.25
	8		8.366	29.46
	2	40	14.57	1.88
	4		13.265	10.67
	6		12.269	17.38
	8		11.551	22.21
	2	50	19.106	1.26
	4		17.921	7.38
	6		16.627	14.07
	8		16.072	16.94

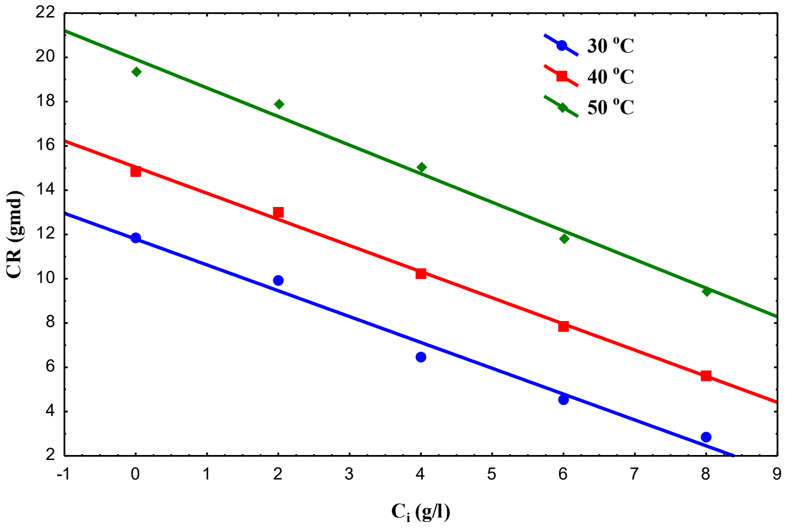


Fig.(1): Concentration of (NPHA) effect on the Copper alloy Corrosion Rate in Hydrochloric Acid at different Temperatures.

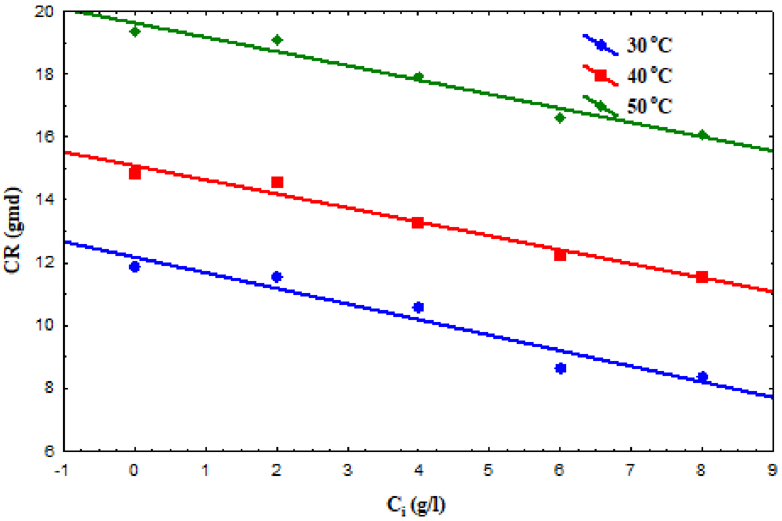


Fig.(2): Concentration of (PHDA) effect on the Copper alloy Corrosion Rate in Hydrochloric Acid at different Temperatures.

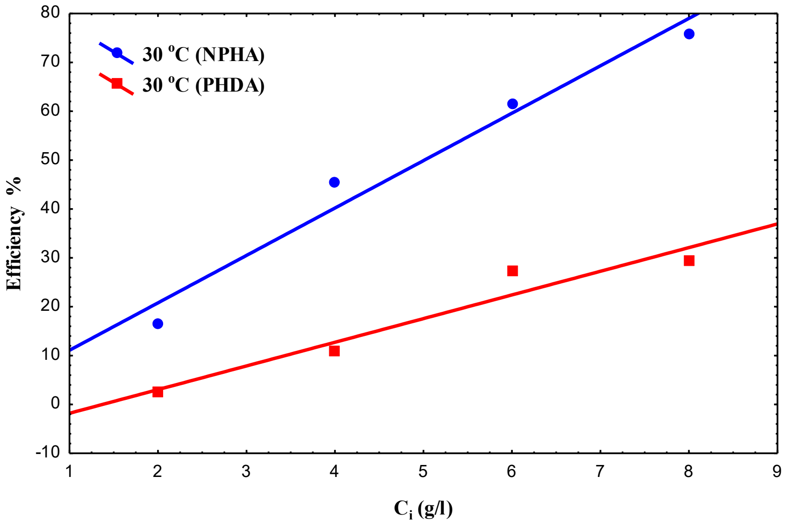


Fig.(3): Efficiency of Inhibitors (NPHA & PHDA) Vs. Inhibitors Concentration at 30 °C.

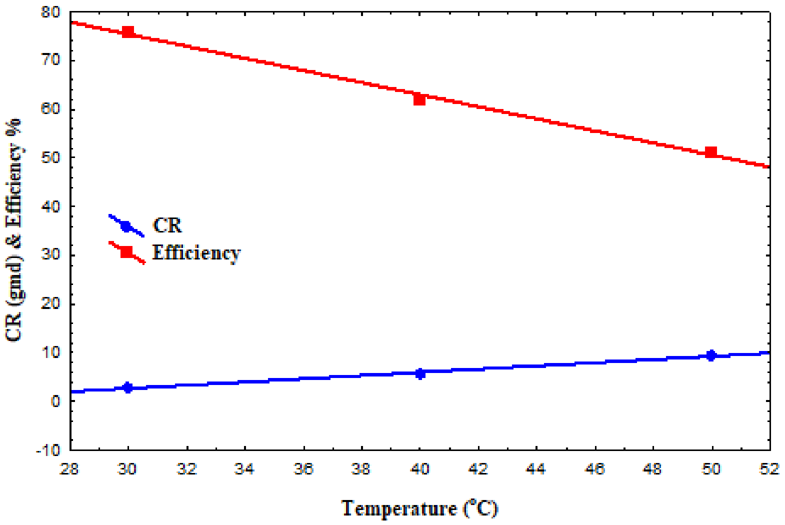


Fig.(4): Temperature effect on the Corrosion Rate & Efficiency of Copper alloy in corrosive medium in presence of (8 g/l) from NPHA.

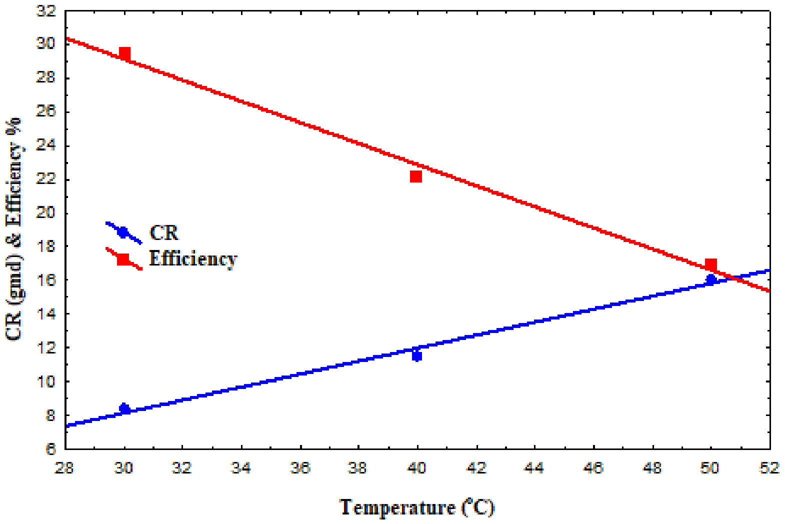


Fig.(5): Temperature effect on the Corrosion Rate & Efficiency of Copper alloy in corrosive medium in presence of (8 g/l) from PHDA.

3.2. Influence of temperature and thermodynamic parameters

In acidic conditions (the appearance of hydrogen), corrosion rates increase exponentially with temperature (Yıldırım and Cetin, 2008). Activation parameters for various systems may be predicted using (Eq. 3), which represents an Arrhenius equation (Larouj et al., 2015; Larouj et al., 2016; Umoren and Ebenso, 2007).

$$CR = A \exp(-Ea/RT) \qquad (3)$$

The exterior coverage (θ) data are quite salutary while debating the adsorption mechanism. When the exterior surface section is enveloped or covered is deemed as a function of an important variable which is the concentration of preventers or inhibitors at a fixed temperature. The degree of exterior surface coverage with the inhibitor was deemed equal to its degree of protection. This inference is based on the presumption that the thoughtful inhibitors exhibit mainly a blocking mechanism of action besides adsorption isotherm could be estimated at equipoise status. There are three adsorption isotherms in the current study that were used, Eq.4 and Eq.5 symbolize the Langmuir and Freundlich adsorption isotherm, and Eq. 6 symbolize the kinetics–thermodynamics isotherm. The portion covered by the inhibitor on the surface strongly counts on its degree of protection. This conclusion is drawn by the ability of inhibitors associated with the hindrance of corrosion.

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

$$\mathrm{Ln}\theta = \ln K_F + n \ln C \quad (5)$$

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

Tokens KL and KF signalize Langmuir and Freundlich adsorption isotherms, which represent the equilibrium constants. Whereas n is a constant of strength or power in Freundlich adsorption isotherm. In Eq. 6, y signalizes the number of the molecules of preventer filling one effective site and K´ is a constant. Equipoise constant conforming to adsorption isotherm is offered by k = k´1/y. Values of y >1 encompass the inhibitor multilayer figuration on the mineral surface whilst values of y < 1 encompass inhibitor molecules that will take more than one efficacious spot. Two common adsorption isotherms mentioned above illustrate the adsorption mechanism, which is Langmuir and Freundlich. It is noticed that NPHA follows the Freundlich Adsorption Isotherm, whereas PHDA obeys none of the two aforesaid adsorption isotherms. Eq.4 – 6 can be illustrated diagrammatically as shown in Fig. 6, 7, 8, and 9. Table 2 gathers the parameters for all the above-mentioned adsorption isotherms that were acquired.

Table 2 Adsorption parameters of NPHA and PHDA.

Inhibitors	**T(°C)**	**isotherm of Langmuir**		**Isotherm of Freundlich**		**isotherm of Kinetics**		
NPHA		KL(L/ml)	$\Delta°G_{ads.}$(KJ/mol)	KF(L/ml)	n″	Ci(g/l)	Ln A	Ea(KJ/mol)
	30	11.1992	16.2059	0.08375	0.90514	0	2.31647	44.5416
						2	2.45219	54.1520
						4	2.72314	77.4979
						6	2.81023	87.5319
						8	2.99098	109.298
PHDA	30	81.5934	21.2087	0.00785	0.54068	2	2.33496	45.7921
						4	2.36352	48.0817
						6	2.52338	59.8378
						8	2.51513	59.4735

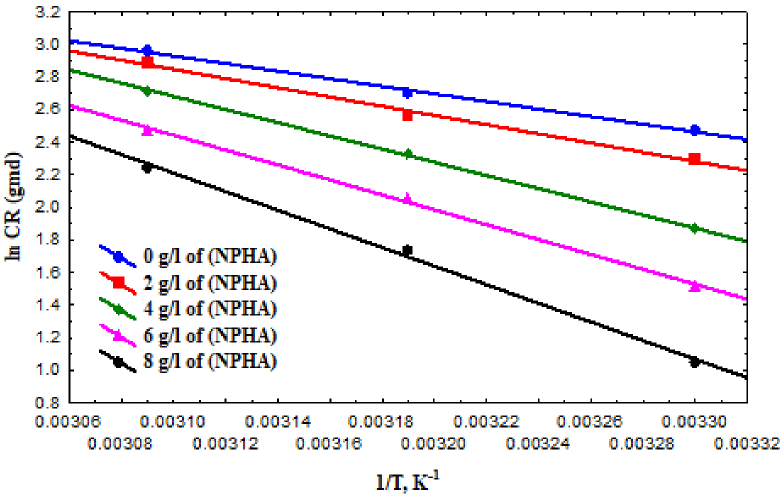


Fig.(6): Arrhenius plot of Copper alloy in Hydrochloric Acid containing various concentration of (NPHA) that effect on the corrosion rate at different Temperature.

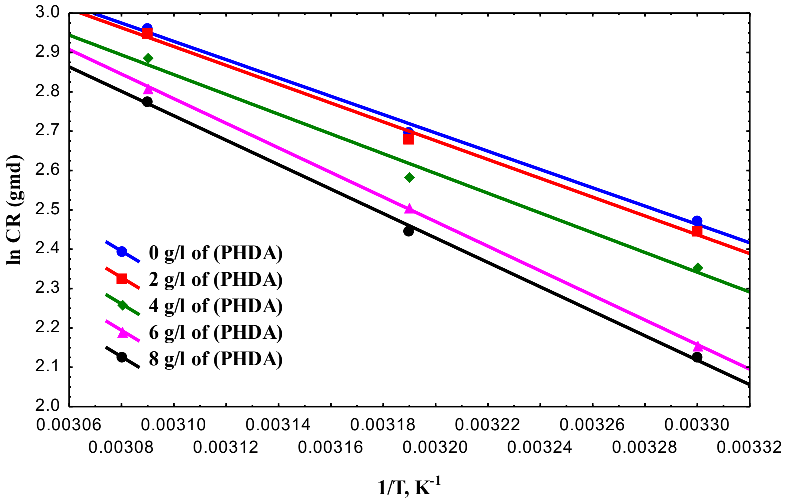


Fig.(7): Arrhenius plot of Copper alloy in Hydrochloric Acid containing various concentration of (PHDA) that effect on the corrosion rate at different Temperature.

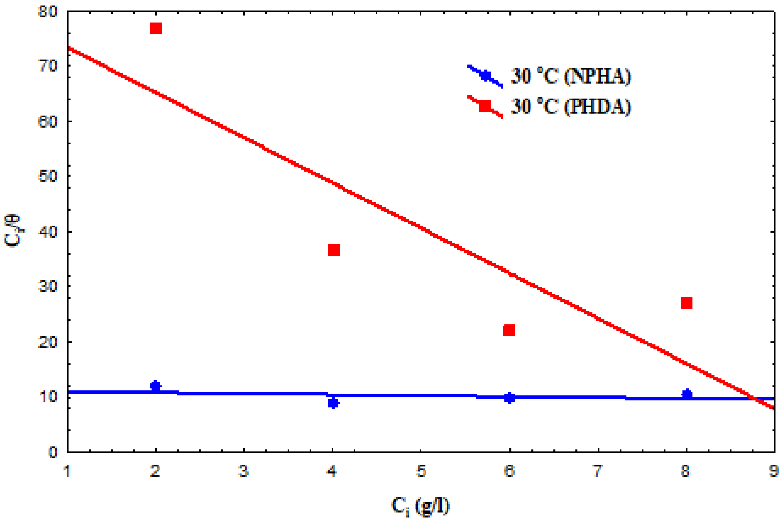


Fig.(8): Langmuir adsorption isotherm of (NPHA) & (PHDA) on the corrosion rate of Copper alloy in Hydrochloric Acid.

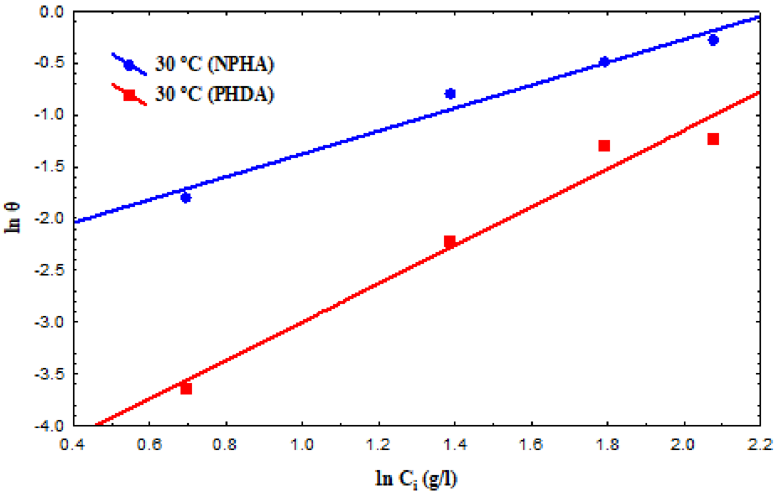


Fig.(9): Freundlich adsorption isotherm of (NPHA) & (PHDA) on the corrosion rate of Copper alloy in Hydrochloric Acid.

4. CONCLUSION

Naphthylamine (NPHA) is more effective than Phenylenediamine (PHDA) as an inhibitor to prevent copper corrosion in (3.5 %) hydrochloric acid environment. The grade of surface coverage with the inhibitor was considered equal to its degree of protection. The efficacy of inhibitor augments with augmenting inhibitor concentration and diminishing of temperature. The highest inhibition efficiency for (NPHA) and (PHDA)were (75.89 %) & (29.46 %) at the higher preventer concentration of (8 g/l) and the temperature of the solution at 30 °C. The results show that the Freundlich Adsorption Isotherm applies to the adsorption of the NPHA inhibitor on the mineral's exterior surface, whereas PHDA does not obey the two previously mentioned adsorption isotherms. Inhibitors that included nitrogen in their composition were recorded as effective inhibitors of corrosion. The Naphthylamine can adsorb on the mineral's total surface. Our research focuses on this type of material as corrosion inhibitors.

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COLLISION OF INTEREST

There is noCompeting benefit emerging from the sharing of other parties, whether interior or exterior to the University.

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