



Novel 1, 2, 4-Triazole Derivatives as Corrosion Inhibitors for Copper in HNO₃ Solution

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Abstract

In our research, organic derivatives were utilized as an eco-friendly green inhibitor to prevent Cu dissolution in 1 M of HNO₃. This study was carried out using chemical methods such as mass loss method (ML), potentiodynamic polarization (PP), and impedance (EIS) techniques. The results obtained from these methods showed that with increasing the concentration of these substances and the inhibition efficiency (%IE) increased and reached to 95.1%. The adsorption of these derivatives on the copper (Cu) surface was used to explain the inhibition. The inhibitors were of mixed kind, according to the polarization curves. It was found that these derivatives follow Langmuir adsorption isotherm. Several surface inspection methods (Scanning electron microscope (SEM), EDX and Fourier transform infrared spectroscopy (FT-IR) have been used. It was found that all of these used methods are in agreement with each other.

Keywords: Cu, HNO₃, 1,2,4-triazole derivatives, SEM, FTIR.

Introduction

In Earth's crust, copper is the third most widely abundant element, accounting for about eight percent of the mineral components [1, 2]. "The importance of Cu metal and its alloys due to its multiple applications in several fields of industries: the food industry, electronic devices, building, and transport, etc. [3, 4]. These different applications depend on several reasons as their low price, their high energy density, and their electrical capacity. Copper metal can form a thin stable oxide layer on it, but in the case of the existence of aggressive media, HNO₃, this stable layer is destroyed and the corrosion will begins [5]. The use of inhibitors is the most practical method for defending against the successive dissolution of metal by corrosion. The use of O, S, and N-containing organic compounds to minimize metal corrosion has been studied [6]. The presence of hetero atoms in the inhibitor's chemical structure plays a significant role in the action of corrosion inhibition. Other factors have a significant influence on the efficiency of inhibition, such as molecular weight, aromatic rings, and inhibited metal load [7-

13]. Furan and thiophene compounds have been recently reported for their corrosion inhibition effects [14] and described with a wide range of biological potential as anticancer agents [15], antimutagenic agents [16], and antimicrobial activities [17]. Heterocycle-containing pyrimidines are safe inhibitor at some degree of concentrations have excellent corrosion inhibition effects on copper metal in acidic media" [18, 19].

As a result, utilizing "ML and electrochemical techniques, the current research describes a study of the corrosion protective activity of organic derivatives on Cu corrosion in 1M nitric acid solution. The inhibition efficiency at different concentrations of inhibitors in acidic media was investigated and discussed. Temperature effects on Cu dissolving in free and inhibited acid solutions were also investigated".

2. EXPERIMENTAL

2.1 Materials and solution:

The samples of copper were cut out from a copper sheet with chemical composition "(wt. %) 0.0023 Pb,

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0.005 Zn, 0.0023 P, 0.004 Ni, 0.0018 Al, 0015 Si, 0.0011 S, Co 0.0019, and rest Cu. In this experiment, the nitric acid that was used (5 M) was prepared from 70% nitric acid using dual distilled water, afterward, its concentration was checked. Using the prepared HNO₃, different solutions containing 2 M HNO₃ were prepared, without or by adding different concentrations from 4x10⁻⁶ to 24x10⁻⁶ M”.

The organic compounds have been investigated. “The used organic are chosen for this work as Cu inhibitors because they have high solubility in water, have high molecular mass, and have many donating atoms. 10⁻³M stock solutions from the studied inhibitors were prepared by dissolving the convenient weights of the organic compounds in bidistilled water; the other concentrations of compounds (4x10⁻⁶ to 24x10⁻⁶M) were prepared by dilution with bidistilled water.

All the materials used were of AR grade and used as received”. The structure formulas of the examined inhibitors are given in Table 1.

2.2 Mass Loss (ML) Measurements:

ML measurements use “Cu coupons with dimensions 2cm x 2cm x 0.2 cm in 1.0 M HNO₃ solution with various doses of the prepared organic compounds. The coupons were abraded with emery papers of different grit sizes (1000, 1500, and 2000) then washed, dried, weighed, and suspended in 100

ml HNO₃ solution without and with various doses of the studied compounds for 3 hours at 25°C, 30°C, 40°C, and 45°C. After a particular time, the Cu coins were removed from the aggressive solution, washed using bidistilled water, dried, and weighed”

2.3 Electrochemical measurements:

“Electrochemical experiments used Cu specimen which used in WL technique mounted in glass rod with 1cm² area. The Cu electrode was attached to the glass with an epoxy resin. The electrochemical techniques were performed in a conventional three-electrode glass cell with Cu specimen as working electrode, platinum sheet as counter electrode, and (SCE) as reference electrode. The Cu electrode was treated as in ML measurements, the working electrode was left to stabilize for 30 min before starting the measurements. For PP the electrode potential changed from -800 to +600 mV vs open circuit potential (E_{OCP}) with a scan rate of 1 mVs⁻¹. EIS measurements experiments were carried out in the frequency range of 0.1 Hz to 10 m Hz with amplitude 5 mV” at open circuit potential (OCP) [20-21].

All the electrochemical tests were carried out using (Potentiostat /Galvanostat/ZRA (Gamry PCI 300/4)) and Gamry Echem Analyst software 5.1 was used for fitting data.

Table (1): Chemical structures of the prepared organic compounds

Names	Structures
(A)	<p>5,5'-disulfanediyldis(3-(4-methoxyphenyl)-4H-1,2,4-triazol-4-amine) Chemical Formula: C₁₈H₁₈N₈O₂S₂ Exact Mass: 442.10 Molecular Weight: 442.52 m/z: 442.10 (100.0%), 443.10 (19.5%), 444.10 (9.0%), 443.10 (3.0%), 444.11 (1.8%), 445.10 (1.8%), 443.10 (1.6%) Elemental Analysis: C, 48.86; H, 4.10; N, 25.32; O, 7.23; S, 14.49</p>
(B)	<p>3-((2,4-dinitrophenyl)thio)-5-(4-methoxyphenyl)-4H-1,2,4-triazol-4-amine Chemical Formula: C₁₅H₁₂N₆O₅S Exact Mass: 388.06 Molecular Weight: 388.36 m/z: 388.06 (100.0%), 389.06 (16.2%), 390.05 (4.5%), 389.06 (2.2%), 390.07 (1.2%), 390.06 (1.0%) Elemental Analysis: C, 46.39; H, 3.11; N, 21.64; O, 20.60; S, 8.26</p>

2.4 Surface Examinations:

2.3. Surface examination techniques

These methods were studied by abrading the Cu coins, “washing with bi-distilled water and acetone. After dipping for one day in 1 M HNO₃ without and with 24x10⁻⁶ M at 25°C, the coins were removed, cleaned with bi-distilled water, then dried, these coins were used for all tests of surface examination”.

2.3.1. Surface morphology investigation by SEM and EDX techniques

Scanning electron microscopy (SEM) model “A Jeol JSM-5400 instrument was used in the investigation. Furthermore, the copper samples were analyzed using the energy dispersive X-ray (EDX) spectroscopy system supplied (Zeiss Evo 10 instrument model). The voltage of the beam accelerating was 25 kV”.

2.3.2. Fourier transform infrared spectroscopy (FT-IR) tests

The function groups of the inhibitor molecules were investigated. “Mansoura University used an FT-IR spectrophotometer (Model 960 Moog, ATI Mattson Infinity Series, USA) to get an infrared spectrum”.

3. RESULTS AND DISCUSSION

3.1. ML measurements:

“ML tests were achieved at different temperatures to explain the inhibition mechanism and to determine the thermodynamic parameters of the corrosion process. This study was carried out at different time intervals in nonexistence and existence of various doses of the prepared compounds. The relation of ML with time was represented in Figure (1) for compound (A), the most effective one. The same curves of compound (B) were obtained (not shown). From these curves, one can found that the curves in the presence of inhibitors lies below the free acid curve. In presence of inhibitors, there is a decrease in ML and an increase in the inhibition efficiency with increasing the inhibitor dose. The results confirm that these organic compounds are good corrosion inhibitors for Cu in 1 M HNO₃”. The (%η) were determined from equation (1).

$$\% \eta = \theta \times 100 = \left(1 - \frac{\Delta W_u}{\Delta W_i}\right) 100 \quad (1)$$

where “ΔW_u and ΔW_i are the weight losses per unit area with and without the inhibitor, respectively. The values of corrosion rate (CR) and %η were obtained for studied compounds at different doses and at 25°C and are summarized in Table (2). The study revealed that, the inhibiting effect of compound (A) is higher than the inhibiting effect of compound (B) at the same doses”.

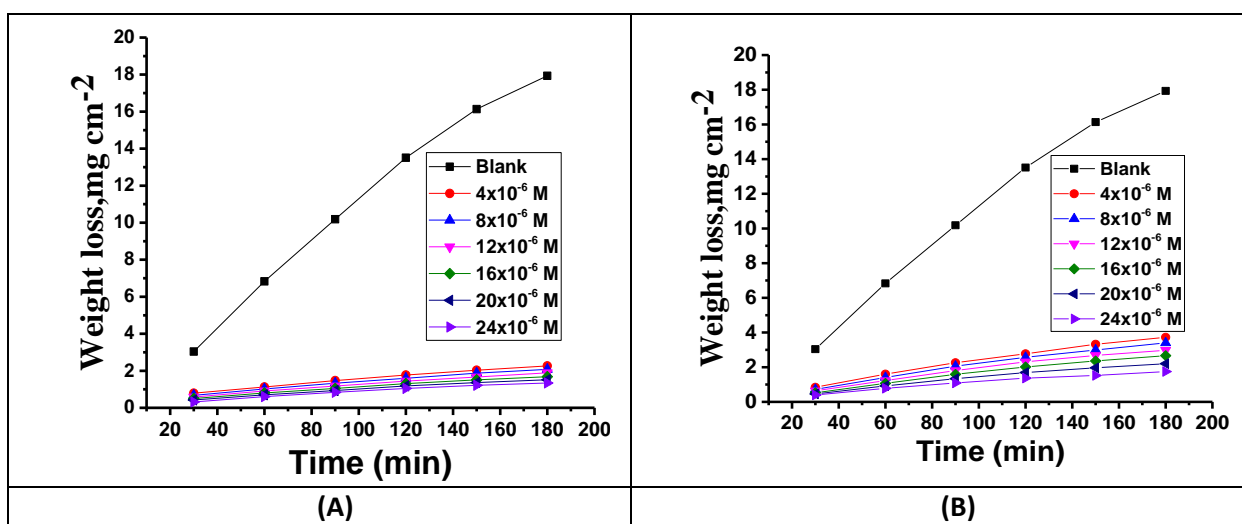


Fig (1): ML-time curves for the dissolution of Cu without and with different doses of compounds (A and B) in HNO₃ at 25°C

Table (2): Corrosion Rate (CR) and inhibition efficiency (% η) from ML measurements with different doses of studied organic compounds after 120 min immersion at 25°C

Conc., Mx10 ⁶	A		B	
	CR mg cm ⁻² min ⁻¹	% η	CR mg cm ⁻² min ⁻¹	% η
0.0	0.14259	--	0.142595	--
4	0.01586	88.9	0.023632	83.4
8	0.01384	90.3	0.022055	84.5
12	0.01282	91.0	0.019128	86.6
16	0.01170	91.8	0.017777	87.5
20	0.01057	92.6	0.014624	89.7
24	0.00990	93.1	0.012034	91.6

3.2 Adsorption isotherm:

“The mechanism of inhibition can be explained by adsorption of organic molecules on metal where the inhibitor molecules replaced the water molecules adsorbed on the Cu surface. The surface coverage of different doses of the inhibitors has been determined from ML measurements. The relation of (θ) with inhibitor concentration was tested graphically by fitting to various adsorption isotherms. The perfect fit was found to obey Langmuir model (Eq.2) with correlation coefficient ($R^2 > 0.99$)” as shown in Figure (2).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (2)$$

where “C is concentration (mol L⁻¹) of inhibitor, θ is the degree of surface coverage and K_{ads} is the adsorption equilibrium constant. The free energy of adsorption ΔG°_{ads} can be calculated using equation” (3).

$$K_{ads} = \frac{1}{55.5} \exp[-\Delta G^{\circ}_{ads} / RT] \quad (3)$$

where “55.5 is the molar dose of water in M⁻¹. The ΔG°_{ads} was determined using Eq. (3) where one molecule of water is replaced by one molecule of inhibitor [22]. The values of ΔG°_{ads} and K_{ads} are given in Table (3). According to the Van't Hoff equation the adsorption power, ΔH°_{ads} , can be determined from the slope of the relation of $\log K_{ads}$ (4)

The standard entropy of ΔS°_{ads} for adsorption can be determined from the following equation according to thermodynamics:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad (5)$$

The adsorption of organic compounds on the metal surface is a spontaneous process and stable as obtained from “ ΔG°_{ads} values. The ΔG°_{ads} values can determine the type of adsorption, if ΔG°_{ads} values are around -20 kJ mol⁻¹ or less negative that refers to the

adsorption is physisorption and if the values are around - 40 kJ mol⁻¹ or more negative that refers to chemisorption process [23, 24]. In the present study, the calculated values of ΔG°_{ads} of these inhibitors reported in Table (3) are 21.3-24 kJ mol⁻¹ or less which confirmed that the adsorption of these compounds on Cu is physisorption process. The investigated compounds have good inhibition efficiency as obtained from the values of K_{ads} where the high values of K_{ads} indicates strong electrical interaction between the adsorbed organic compounds molecules on the metal surface. On the other hand, the small values of K_{ads} indicates that the interactions between the adsorbed molecules and the metal surface are weaker”, and as a result, the compound molecules are easily replaced by the solvent molecules from the metal surface [25].

3.3 Kinetic and thermodynamic parameters:

“The corrosion process is considered as chemical reaction in which the atoms at metal surface react with the negatively charged anions (OH⁻, SO₄²⁻, NO₃⁻, etc.) of the environment. Like any other chemical reaction, temperature is an important factor that influence the rate of corrosion reaction. During elevating the temperature of the medium, the activation energy of atoms at the metal surface will increase and this will reduce the corrosion reaction of the metal in the acidic medium. The influence of temperature on the corrosion rate of metals can express by Arrhenius equation” [26].

$$k_{corr} = A e^{-E_a^*/RT} \quad (6)$$

where A is pre-exponential factor and E_a^{*} is activation energy.

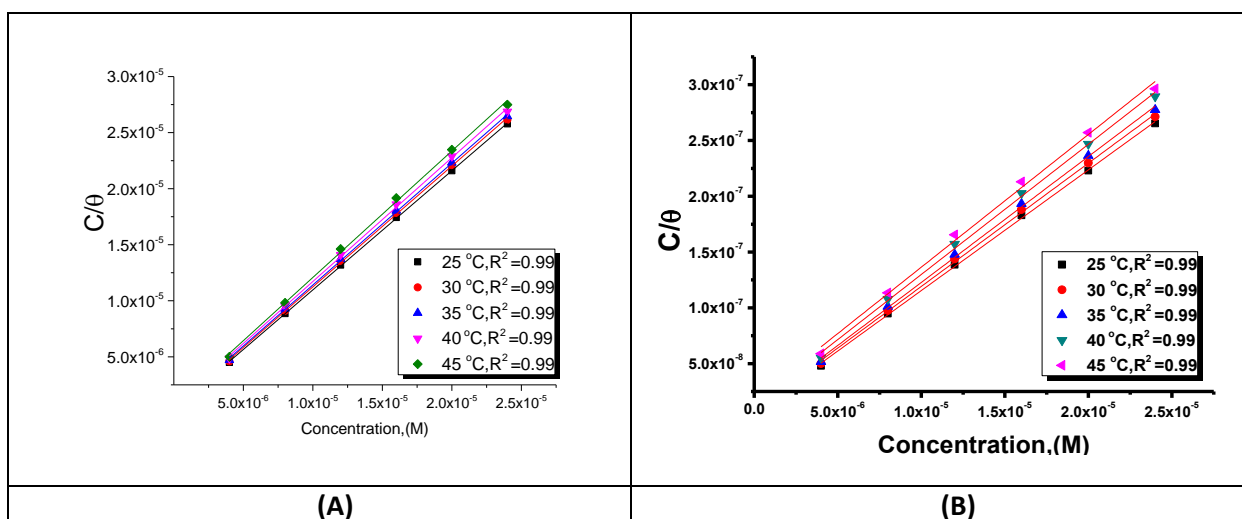


Fig (2): Langmuir adsorption model as (C/θ) vs. C of the adsorption of compounds (A and B) on Cu in 1M HNO₃ at various temperature

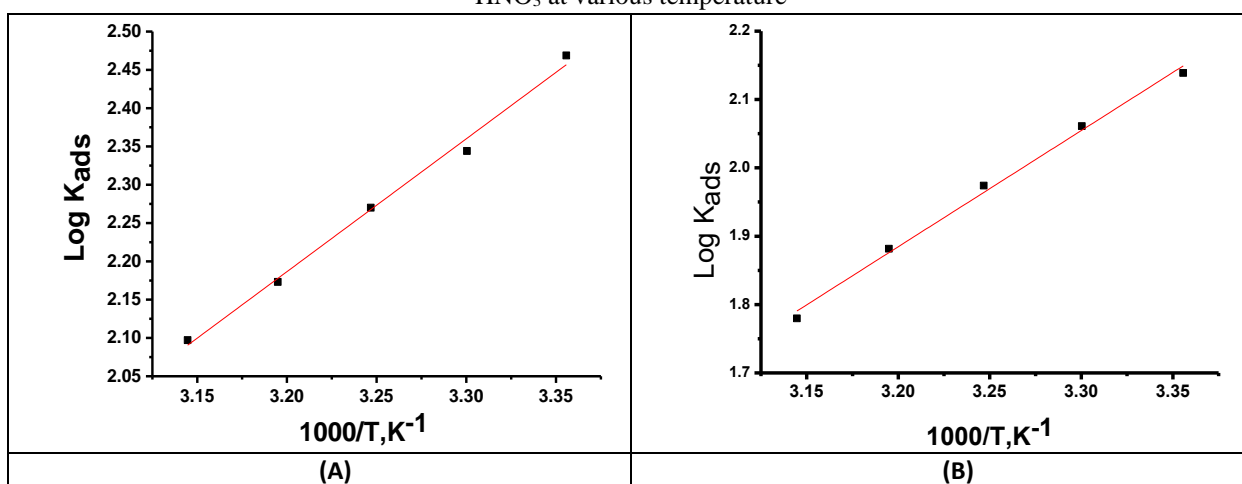


Fig (3): Plot of variation of $\text{Log } K_{\text{ads}}$ vs. $1/T$ for the adsorption of various doses of compound (A and B) on the (Cu) surface in 1.0 M HNO₃ at different temperatures.

Table (3): K_{ads} and $\Delta G^{\circ}_{\text{ads}}$ for the adsorption of organic compounds on Cu in 1M HNO₃ from ML method at 25°C

Compound	Temp. °C	K_{ads} M ⁻¹	$-\Delta G^{\circ}_{\text{ads}}$ kJ mol ⁻¹	$-\Delta H^{\circ}_{\text{ads}}$ kJ mol ⁻¹	$-\Delta S^{\circ}_{\text{ads}}$ J mol ⁻¹ K ⁻¹
A	25	294	24.0	33	80.5
	30	220	23.7		78.1
	35	186	23.6		76.7
	40	149	23.4		74.9
	45	125	23.3		73.4
B	25	140	22.2	32	74.3
	30	115	22.1		72.7
	35	101	22.0		71.7
	40	76	21.7		69.3
	45	57	21.3		66.9

“Plots of $\log(k_{\text{corr}})$ against $(1/T)$ for Cu immersed in 1 M HNO_3 without and with various doses of organic compounds are presented in Figure (4). E_a^* can be calculated from the slope of these lines, the calculated data represented in Table (4). ΔH^* and ΔS^* of the corrosion reaction are obtained from the transition state equation as”:

$$k_{\text{corr}} = \frac{RT}{Nh} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (7)$$

Where “h” is Planck’s constant. A plot of $\log(k_{\text{corr}}/T)$ vs. $(1/T)$ for Cu in 1 M HNO_3 with different doses of the inhibitor gives straight lines as represented in Figure (5), ΔH^* and ΔS^* were calculated using the slopes and intercepts of lines and their values are summarized in Table (4). The calculated values in Table (4) showed that, activation

energy of Cu increase with adding the inhibitor to the medium which powerfully adsorbed on the metal surface and increases the energy barrier of the corrosion reaction as the inhibitor concentration increased. Physisorption is accompanied by the formation of a protective film on metal surface and that what explain the growing of activation energy values with increasing inhibitor doses [27]. The positive values of ΔH^* referred to the corrosion reaction is endothermic reaction. The entropy of activation is large and negative. This indicated that the activated complex represents the association step not the dissociation step”, causing a decrease in disorder occurs from reactants to the activated complex [28].

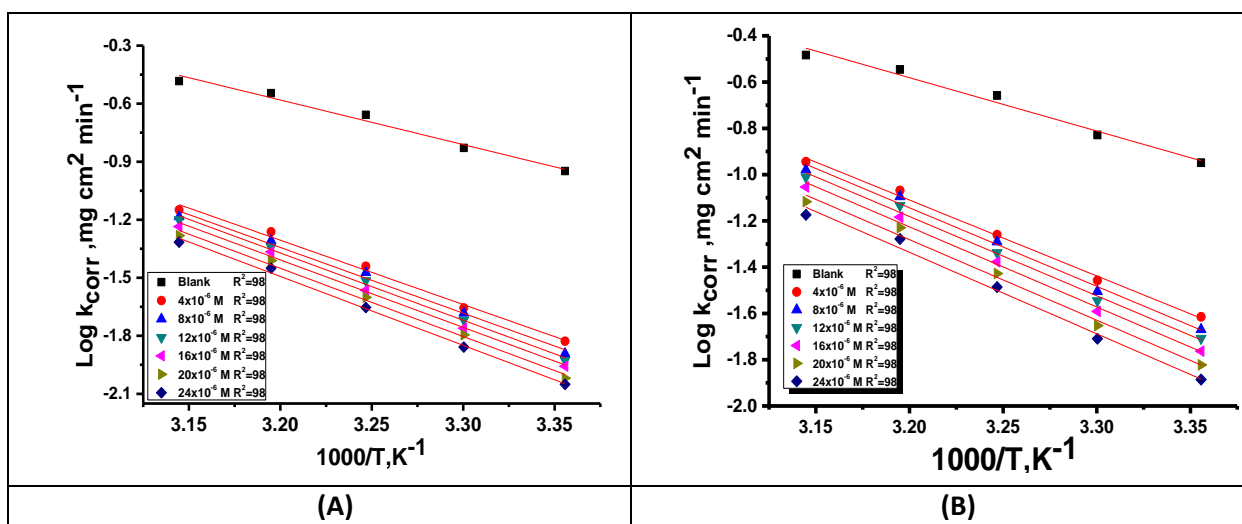


Fig (4): $\log(k_{\text{corr}})$ vs. $1/T$ of Cu corrosion in 1 M HNO_3 without and with several doses of inhibitors (A and B)

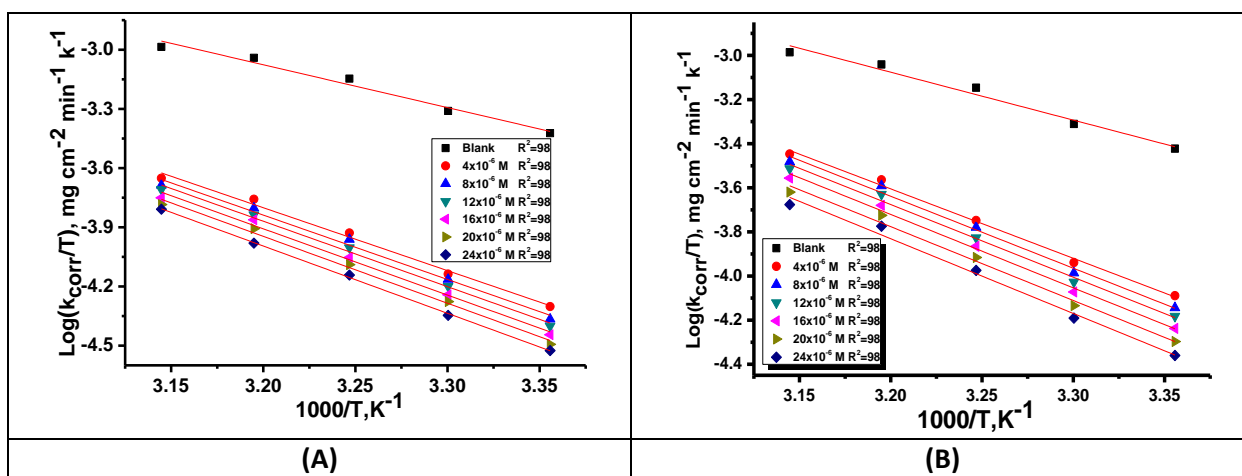


Fig (5): $\log(k_{\text{corr}}/T)$ vs. $1/T$ of Cu corrosion in 1 M HNO_3 without and with several doses of inhibitors (A and B)

Table (4): Activation parameters of Cu corrosion in 1 M HNO₃ without and with several doses of investigated compounds

Conc., Mx10 ⁶	E _a [*] kJ mol ⁻¹	ΔH [*] kJ mol ⁻¹	-ΔS [*] J mol ⁻¹ K ⁻¹
Blank	45.4	41.6	122.1
A			
4	64.9	62.2	73.7
8	66.3	63.6	69.9
12	67.8	65.1	67.1
16	68.0	65.5	65.4
20	68.8	66.1	64.1
24	69.5	66.7	63.5
B			
4	64.0	61.4	71.8
8	66.2	63.6	65.8
12	66.8	64.5	64.8
16	67.5	64.9	62.8
20	67.8	65.2	62.8
24	68.7	66.2	61.8

3.4 Electrochemical measurement

3.4.1 PP method:

“Tafel plots of the studied organic compounds were obtained from polarization curves. Figure (6) shows the PP diagrams of Cu in 1.0M HNO₃ in the existence and nonexistence of altered doses of inhibitor (A). Similar curves were obtained for compound (B) (not shown). PP curves showed that the current density of both the anodic and cathodic reaction shifted towards lower values as the inhibitor dose increase. The parameters obtained from PP technique (*i*_{corr}), (*E*_{corr}), (β_a), (β_c), and (% η) deduced from the curves are listed in Table (5). The inhibition efficiency (% η) can be calculated using the (*i*_{corr})

values determined by Tafel extrapolation [29] as follows”:

$$\% \eta = \left[1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \right] \times 100 \quad (8)$$

where “*i*_{corr}⁰ and *i*_{corr} are the current densities of uninhibited and inhibited solution, respectively”.

The corrosion potential displayed small change in the range ± 27 mV around the corrosion potential of -19 mV. “These results clarified that the presence of inhibitors effect both Cu dissolution and cathodic reaction; accordingly these inhibitors act as mixed kind inhibitors. Data are listed in Table (5) confirmed that the inhibition efficiency of compound (A) is higher than that of compound (B)”.

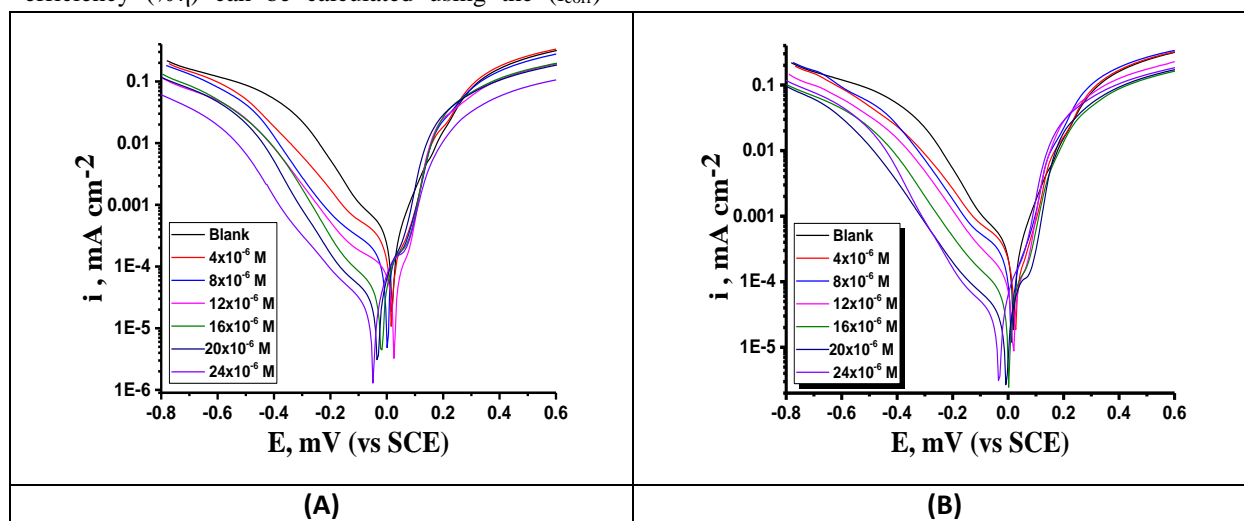


Fig (6): PP diagrams of liquefaction of Cu in 1.0M HNO₃ without and with different doses of inhibitor (A and B)

Table (5): Data from PP technique for the corrosion of Cu in 1 M HNO₃ at several doses of prepared compounds at 25°C

Inh.	Conc., Mx10 ⁶	<i>i</i> _{corr} , μA cm ⁻²	<i>E</i> _{corr} , mV vs SCE	β _a , mV dec ⁻¹	β _c , mV dec ⁻¹	C.R mpy	Θ	% η
Blank	0.0	396	19	115	185	381	--	--
A	4	184	17	109	195	177	0.535	53.5
	8	159	11	108	210	144	0.598	59.8
	12	139	26	105	195	122	0.649	64.9
	16	135	-19	98	187	70	0.659	65.9
	20	38	-32	85	205	20	0.904	90.4
	24	26	27	87	199	13	0.934	93.4
B	4	237	25	119	205	262	0.402	40.2
	8	149	12	117	197	143	0.624	62.4
	12	133	18	110	185	139	0.664	66.4
	16	126	29	105	199	137	0.682	68.2
	20	94	-12	95	195	48	0.763	76.3
	24	32	-38	98	200	15	0.919	91.9

3.4.2 EIS method: "EIS experiments were accomplished in acidic medium with and without additives and the electrochemical parameters at 25°C are shown in Figures (7, 8) for compound (A). The double layer capacitance (*C*_{dl}) and %η are calculated from the following equations":

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (9)$$

Where "*f*_{max} refers to the maximum frequency at which the imaginary constituent of the impedance (*Z*_{im}) is higher".

$$\% \eta = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \quad (10)$$

Where *R*_{ct} and *R*⁰_{ct} are resistant in absence and presence of the additives

The circuit that fit the outcome data is displayed in Figure (9). "The extracted data were calculated and tabulated in Table (6). Figure (7) represented the impedance diagrams consist of one large capacitive loop. The addition of inhibitors improves the value of *R*_{ct} in HNO₃ solution. There is

an increase in IE as a result of increasing *R*_{ct} which explained by the replacement of water molecules attached to the metal surface by inhibitor molecules to form a passive layer on Cu surface, this decreases the double layer thickness. It was observed that with increasing inhibitor doses, the double layer capacitance increased, and the local dielectric constant decreased. This can be explained by the adsorption of these derivatives molecules on both anodic and cathodic sites of the surface [30]. The imperfect circuit shape is often due to the inhomogeneity of the metal surface originating from surface roughness [31, 32]. Results obtained from EIS method are similar to those obtained with other

techniques which confirm the good inhibiting behaviour of the prepared compounds. From the data recorded in Table (6), the *i*_{corr} values decrease with inhibitor addition and the % η is greatly growing. (*i*_{corr}) values are decreased in similar way as the values obtained from (PP) studies". The lowering in (*i*_{corr}) follows the same order as that obtained for *C*_{dl} values.

Table (6): EIS data of Cu corrosion in HNO₃ (1.0M) with altered doses of the prepared compounds at 25°C

Inh.	Conc., Mx10 ⁶	<i>R</i> _{ct} , Ω cm ²	<i>C</i> _{dl} , μF cm ⁻²	θ	% η
blank	0.0	23	142	--	--
A	4	130	81	0.823	82.3
	8	215	56	0.893	89.3
	12	351	48	0.934	93.4
	16	428	33	0.946	94.6
	20	436	30	0.947	94.7
	24	564	26	0.959	95.9
B	4	111	90	0.793	79.3
	8	185	85	0.876	87.6
	12	281	54	0.918	91.8
	16	333	48	0.931	93.1
	20	351	33	0.934	93.4
	24	430	27	0.947	94.7

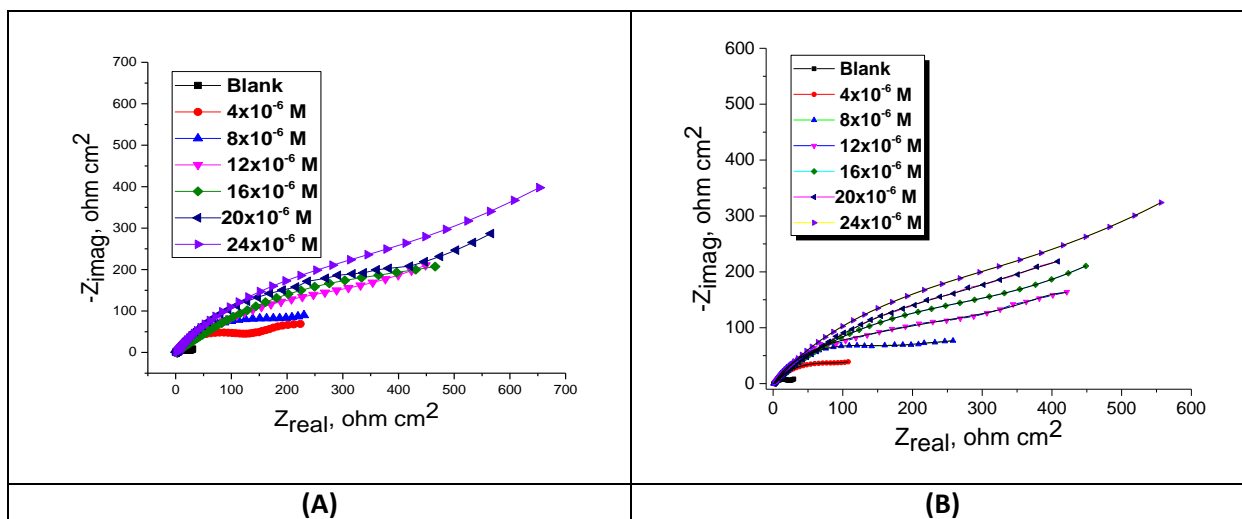


Fig (7): EIS Nyquist diagrams for Cu in HNO₃ (1.0M) in the nonexistence and existence of various doses of compounds (A and B)

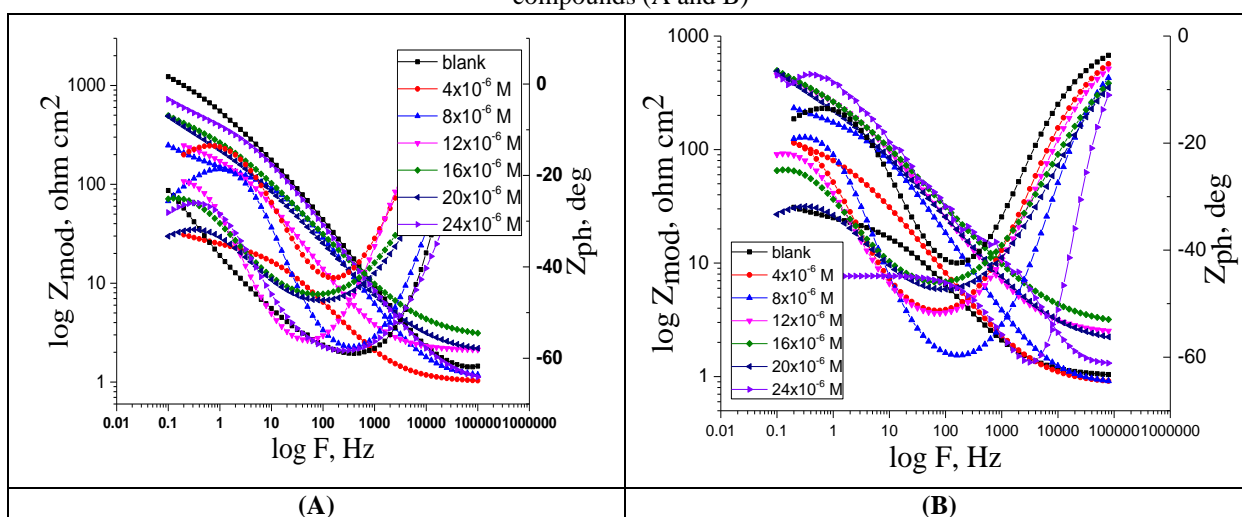


Fig (8): EIS Bode diagrams of Cu in 1 M HNO₃ in the existence and nonexistence of different doses of compound (A)

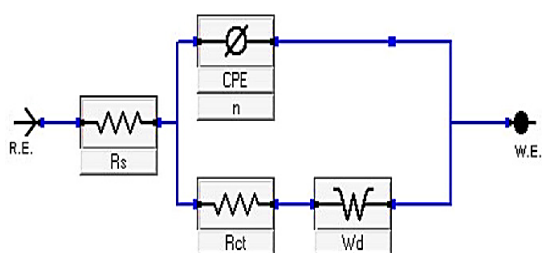


Fig (9): Equivalent circuit utilized to fit the EIS data

3.5 Surface Examinations

3.5.1 SEM analysis:

“The photograph of Cu before immersion in acid solution shows the surface was smooth and without pits. The photograph of Cu after immersion in acid solution shows the surface was strongly attacked by corrosion products. The photograph of

Cu after immersion in acid solution with the maximum concentration of the inhibitors shows the surface of the Cu becomes coated by cracked cover layer, compared with that of free acid and was free from pits and it became smooth. This proves that the investigated compounds are adsorbed on Cu surface forming a thick protective layer, hindering the corrosion process” [33].

3.5.2. Energy Dispersion Spectroscopy (EDX)

“The EDX spectra were used to determine the elements present on the surface of Cu and after 1 day of exposure in 1 M HNO₃ acid with optimum concentration of inhibitor. Figure (11), gives the EDX analysis of Cu in 1.0 M HNO₃ in the presence of 4x10⁻⁶ M organic compounds. The spectra show additional lines, demonstrating the existence of C (owing to the carbon atoms of organic compounds

compound). These data display that the carbon, oxygen, and nitrogen atoms covered the specimen surface. The EDX analysis indicates that only, carbon, oxygen and nitrogen were detected, and shows that the passivation film contained the

chemical formula of organic compounds adsorbed on the surface of Cu. It is seen that, the percent weight of adsorb elements C, O and N were present in the spectra and recorded in Table (7)".

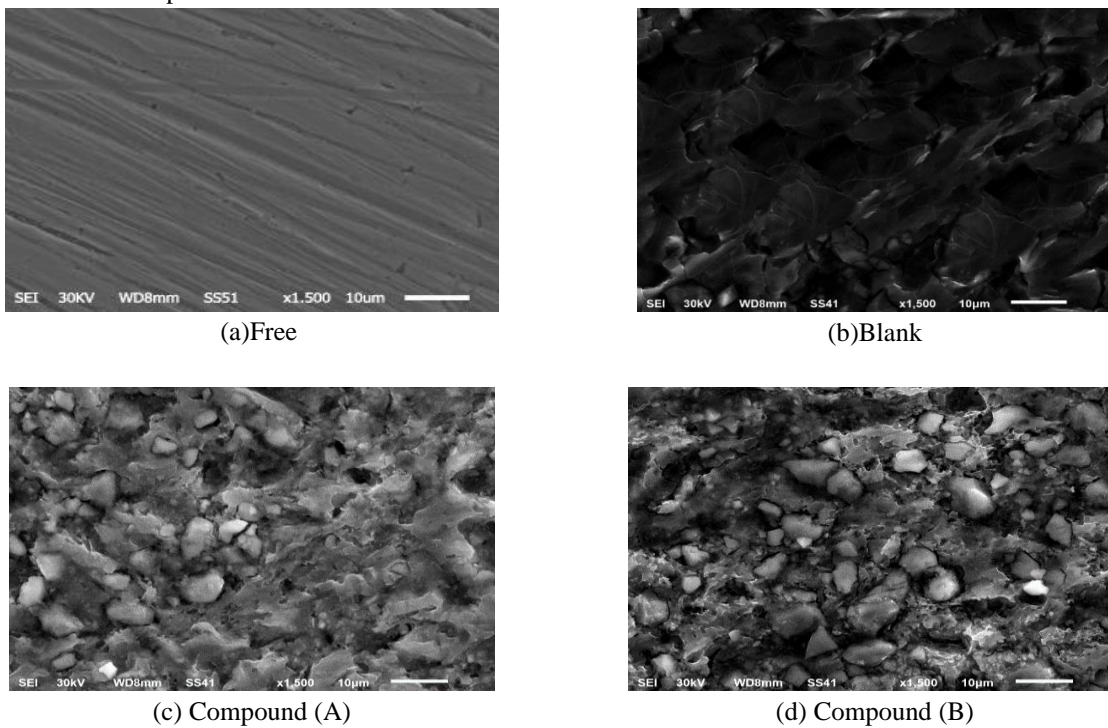


Fig (10): SEM micrographs for Cu immersed in HNO₃ (1.0M) without and with 24×10^{-6} of organic compounds for 1 day

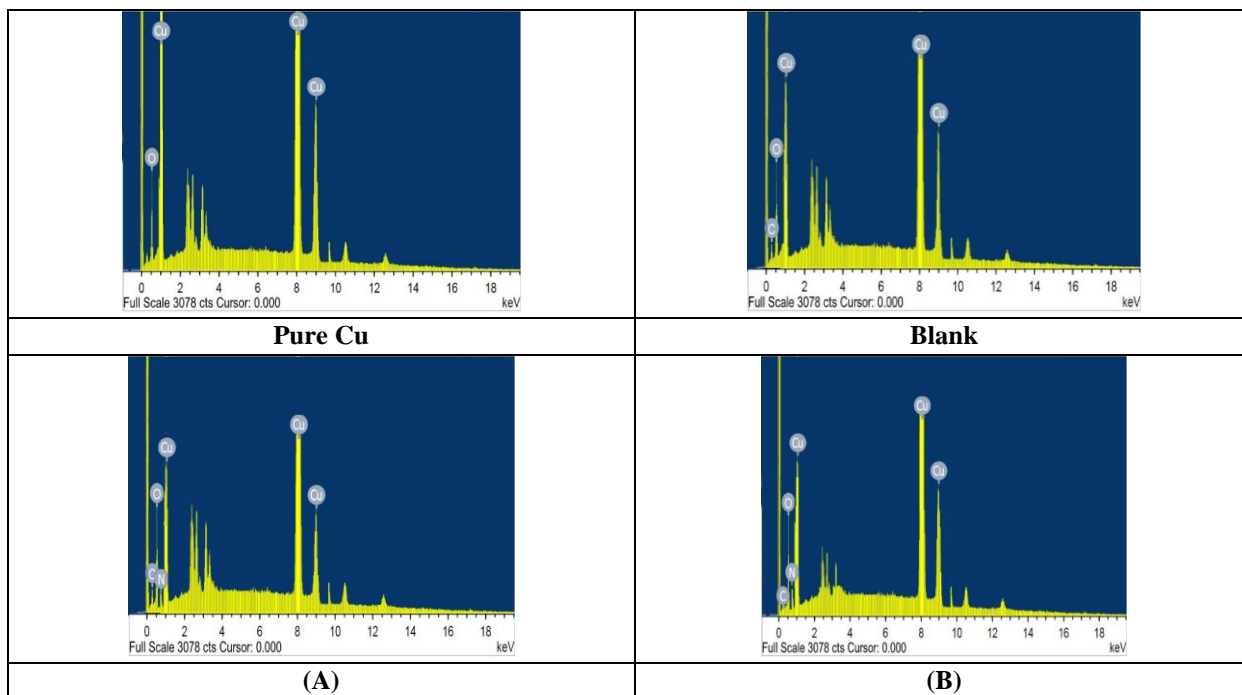


Fig (11). EDX analysis on Cu in the presence and absence of 24×10^{-6} ppm inhibitors for 1-day immersion.

Table (7): Surface composition (% wt) of Cu after one day of immersion in 1M HNO₃ without and with the 24x10⁻⁶ ppm inhibitors

(Mass %)	Cu	C	O	N
Free	98.99	0.89	0.03	-
1M HNO ₃	78.18	15.13	6.69	-
A	62.15	12.1	15.3	10.45
B	66.51	14.5	11.5	7.49

3.5.3. FT-IR technique

“Functional groups and covalent bonding knowledge had been identified by FT-IR which is an influential analytical device [34]. The IR spectra of appeared certain peaks corresponded to the function groups in the investigated compounds. After dipping in 1 M HNO₃ + 24x10⁻⁶ M studied compounds (A) for one day, similar curves were obtained for compound (B) (not shown), and characteristic spectra of compounds A&B and the Cu surface were attained and compared to each other (Figure 12). The data of FT-IR showed that: There is a small shift in the peaks of the inhibitor function groups which adsorbed on the Cu surface and this indicate that these compounds can act as corrosion inhibitors” [35].

3.7. Mechanism of corrosion inhibition

Four kinds of adsorption may occur: “1) Electrostatic attraction among the investigated molecules and Cu; 2) Contact of unshared electron pairs in the investigated derivatives with the Cu; 3) The interaction of metal π -electrons; 4) Summation of all the above. From the outcome data obtained from the various tests, corrosion hindrance of Cu in 1

M HNO₃ solutions by the investigated derivatives as designated from ML, PP, EIS tests depend on the nature of the inhibitor and the dose. These investigated compounds form adsorbed layer on the Cu surface which cover the active sites and decrease corrosion by preventing the attack of the surface by the corrosive medium. The NO₃⁻ ions get adsorbed on the Cu surface and turn it negatively charged surface, the protonated inhibitors molecules (cationic) get adsorbed on the negatively charged surface of Cu physically by an electrostatic attraction [36,37]. The sequence of IE is at A > B. This order of the IE of the tested compounds can be accounted in terms of the molecular size. A > B, this may be due to the greater molecular size”. The utilized investigated derivatives as corrosion protection for Cu in 1 M HNO₃ was deliberated in terms of physical adsorption on the Cu surface.

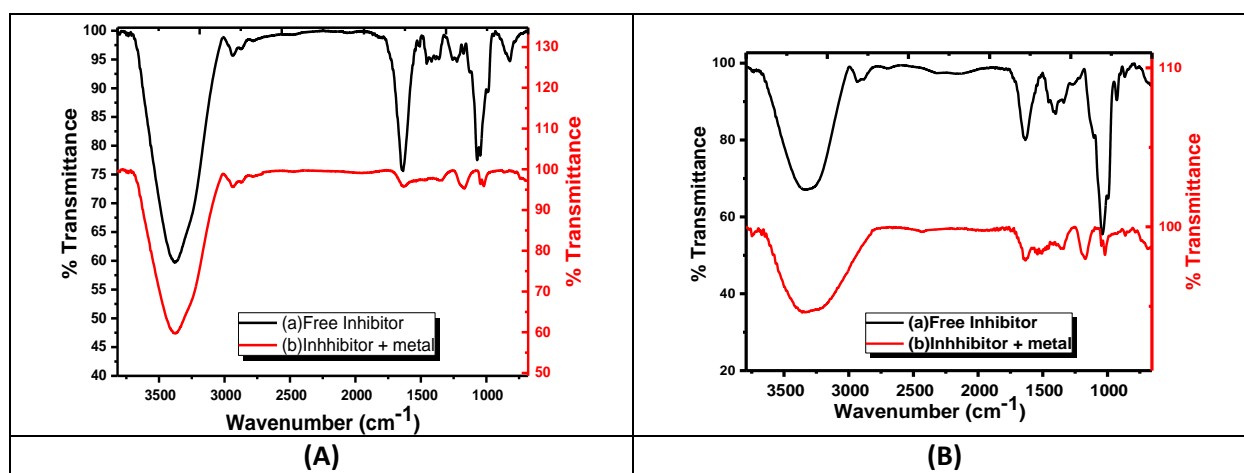
CONCLUSIONS

1- The organic compounds showed good inhibiting efficacy for Cu corrosion in 1 M nitric acid.

2- PP indicated that organic compounds acted as a mixed-type inhibitor.

3- All experimental results, which were obtained from the ML method and electrochemical techniques (PP, and EIS) were consistent with each other.

4- By rising the concentration of organic compounds, the effectiveness of the inhibitor increases, moreover, the inhibitor is inhibited by adsorbing the organic compounds on the Cu surface. Adsorption of the extracted molecules obeyed with the Langmuir isotherms and the adsorption was physical adsorption.

**Fig (12):** FT-IR spectrum of compound (A and B) before and after adsorption on Cu surface

5- Surface analysis (SEM, EDX, and FTIR) confirmed that the inhibitor layer formed on the Cu surface, as this film prevented the dissolution of metal in the HNO₃ solution.

6- It is recommended to use 1, 2, 4-Triazol derivatives as corrosion inhibitors in industry due to its high inhibition efficiency

7- The importance of identifying on environmental friendly corrosion inhibitors is warranted and the current research is more focused towards greener alternatives

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