

# Electrochemical and Surface Characterization Studies of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile Compound on Copper in 2 M HNO<sub>3</sub>

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## Abstract

The corrosion hindrance of Cu in 2.0 M HNO<sub>3</sub> solution by 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile compound has been studied, using Potentiodynamic Polarization (PP), AC Impedance (EIS), Electrochemical Frequency Modulation (EFM) techniques. Also, EIS test was utilized to confirm the corrosion protection mechanism. 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile compound is suggested as a mixed kind inhibitor. SEM and EDX investigations of the Cu in 2.0 M HNO<sub>3</sub> surface revealed that assembles protect Cu from corrosion by adsorption on its surfaces by a forming coating film. Clearly, the assembled mechanisms play a role as a barrier to corrosive solution.

## Keywords

Carbonitrile, Cu, SEM, EDX, EIS, EFM

## 1. Introduction

Copper has varied uses in electronic productions and heat exchangers connection and conductors, pipelines for domestic and production water utilities include water, a conductor in electrical strong lines, gotten its higher conductivi-

ties in thermal and electrical, noble moderately properties and its mechanical workability. Therefore, Cu corrosion and its hindrance in excessive altered solution have been significant in numerous investigators [1]-[10]. The higher information tests for hindrance corrosion are inhibitors utilized to moderate the decrease of beneficial superiority of alloys due to corrosion when they electrochemically attack or chemically by its natural surroundings. The assembly of the inhibitor is one of the main factors that influence the inhibitor/metal interaction [11]. For Cu, which can obtain many-bonds, inhibitor molecules comprise S and N atoms are suggested power. Surrounded by the S, O or N containing organic composite is the heterocyclic structure which has an influence on inhibitors for corrosion of Cu in aqueous solution [12]. Heterocyclic composite counting the group of mercapto has also been introduced as inhibitors for Cu for distinct manufactures uses [13]. Azole assembled contains N atoms, which reply with Cu between the electrons lone pair to obtain complexes (Cu-azole) [14]. These complexes are supposed prevalence to be polymeric in form and nature coating film adherent on the alloy including Cu, which play as a barrier to attraction ions such as Cl. In new papers, numerous thiadiazole investigations [15]-[22] have been noted as excellent inhibitors for Cu and Cu alloys corrosion in distinct aggressive solution. As a result of the toxicity of mostly utilized corrosion hindrance, there is great interest in exchanging harmful inhibitors with helpful non-hazardous [23]. The target of this work is to recognize the 2-amino-6-methyl-5oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-2]quinolone-3-carbonitrile assembled as possible corrosion hindrance for Cu in 2.0 M HNO<sub>3</sub>. From the data given, we could recognize the examined molecule as possible corrosion hindrance for Cu in our laboratory, which examined experimentally by PP, EIS and EFM tests. The surface morphology of protect Cu was evaluated by SEM and EDX techniques.

## 2. Experimental

### 2.1. Composition of Material Samples (See Table 1)

### 2.2. Chemicals and Solutions

Nitric acid (BDH grade) and organic additive.

The organic inhibitor utilized in this study was organic composite [24] (see Table 2).

### 2.3. Tests Utilized for Corrosion Calculations

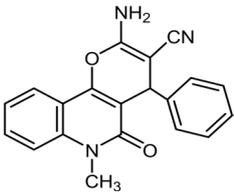
#### 2.3.1. PP Tests

PP tests were accepted in a conformist three-electrode cell with platinum gauze as the auxiliary electrode (1 cm<sup>2</sup>) and a saturated calomel electrode (SCE) as a reference electrode. The working electrode (WE) was in the form of divided cut

**Table 1.** Chemical conformation of the Cu in weight %.

Element	Sn	Ag	Fe	Zn	Pb	As	Cu
Weight %	0.001	0.001	0.01	0.05	0.002	0.0002	The rest

**Table 2.** Chemical structure, name and molecular weight and formula of organic inhibitor.

Structure	Name	Mol. Wt./M. Formula
	2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile	329.35/C <sub>20</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>

from Cu coins of equal arrangement with surface size was 1 cm<sup>2</sup>. Before calculation, the electrode was put in solution at potential for half hours, till a steady state was gotten. The started potential was -600 to +400 mV vs.  $E_{ocp}$ . All tests were done in freshly ready solutions at 30°C and outcome data were always repetitive at minimum three times to check the reproducibility.

### 2.3.2. EIS Tests

Impedance tests were occurred utilizing AC signals of 5 mV signal to signal amplitude at the OCP in the frequency variety of 0.1 Hz to 100 kHz. All impedance values were formfitting to a suitable equivalent circuit utilizing the Gamry Echem Analyst software.

### 2.3.3. EFM Tests

EFM data were achieved with relating potential perturbation signal with amplitude 10 mV with 2 and 5 Hz sine waves [25]. The greater signals were utilized to estimate the current gotten from corrosion density ( $i_{corr}$ ), the Tafel line slopes ( $\beta_c$  and  $\beta_a$ ) and the causality factors CF-2 and CF-3 [26]. All outcome data were obtained utilizing Gamry instrument PCI300/4, DC105 utilize for corrosion software, EIS300 software, EFM140 software and Echem Analyst 5.5 for results drawing, graphing, data correct and measuring.

### 2.3.4. SEM-EDX Analysis

The Cu surface was ready by observance the coins for 3 days in 2.0 M HNO<sub>3</sub> in existence and nonexistence of optimum dose of studied organic composite, after this inundation time, the coins were splashed gently with water bidi-stilled, cautiously dried and mounted into the spectrometer without any extra management. The Cu corroded surfaces were examined utilizing an X-ray diffractometer Philips (pw-1390) with Cu-tube (CuK<sub>α</sub>,  $\lambda = 1.54054 \text{ \AA}$ ) electron microscope utilize for scanning (SEM, JOEL, JSM-T20, Japan).

## 3. Results and Discussion

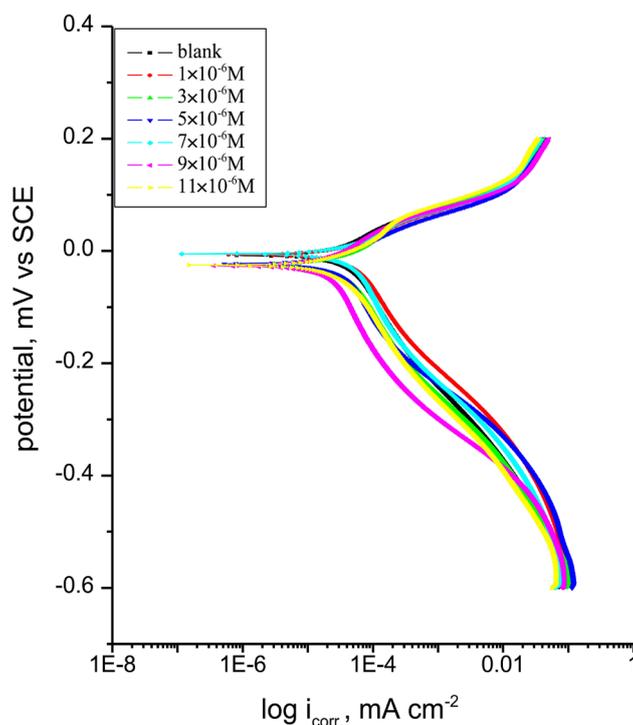
### 3.1. PP Tests

Theoretically, Cu can hardly be corroded in the deoxygenated acid medium, as Cu cannot relocate hydrogen from acid solutions conferring to the theories of chemical thermodynamics [27] [28] [29]. However, these situations will variation in nitric acid. Oxygen dissolved may be reduced on surface of Cu and this

will agree to corrosion to happen. It is a best estimate to negligible the hydrogen liberate reaction and only deliberates reduction of oxygen in the  $\text{HNO}_3$  at potentials adjacent the potentials of corrosion [30].

**Figure 1** demonstrates the PP manner of Cu electrode in 2.0M  $\text{HNO}_3$  in the existence and nonexistence of unlike dose of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile composite. **Figure 1** displays that two anodic reaction and cathodic are influenced by the appending of examined assembled and the protection efficiency improves as the inhibitor dose rise, but the cathodic reaction is more hindrance, significance that the appending of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile composite lower the anodic liquefaction of Cu and also hinders the cathodic reactions. Therefore, studied composite is deliberated as mixed kind inhibitor.

The parameters gotten from electrochemical such as current corrosion densities ( $i_{corr}$ ), potential gotten from corrosion ( $E_{corr}$ ), the cathodic Tafel line slope ( $\beta_c$ ), anodic Tafel line slope ( $\beta_a$ ) and protection efficiency ( $\%IE$ ) were measured from the diagrams (see **Figure 1** and **Table 3**). The outcome data gotten in **Table 3** discovered that the  $i_{corr}$  lower clearly after the appending of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile composite and  $\%IE$  improve with raising the inhibitor dose. In the existence of inhibitor  $E_{corr}$ , was improved with no definite trend, demonstrating that 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile composite play as mixed-kind inhibitor. The  $\%IE$  was measured



**Figure 1.** PP plots for the corrosion of Cu in 2.0 M  $\text{HNO}_3$  in existence and lack of unlike dose of inhibitor at  $30^\circ\text{C} \pm 0.1^\circ\text{C}$ .

**Table 3.** Parameters gotten from PP technique for the corrosion of Cu in 2.0 M HNO<sub>3</sub> at 30 °C ± 0.1 °C.

Compound	Conc. (M)	$E_{Corr}$ (mV vs. SCE)	$i_{Corr} \times 10^{-5}$ ( $\mu\text{A}\cdot\text{cm}^{-2}$ )	$\beta_a \times 10^{-3}$ (mV·dec <sup>-1</sup> )	$\beta_c \times 10^{-3}$ (mV·dec <sup>-1</sup> )	$\theta$	%IE <sub>p</sub>
	Blank	777	92.8	143.4	506.1	----	----
2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile	1 × 10 <sup>-6</sup>	684	83.2	107.8	332.4	0.103	10.3
	3 × 10 <sup>-6</sup>	251	58.4	99.8	352.1	0.370	37.0
	5 × 10 <sup>-6</sup>	232	51.7	97.8	346.0	0.442	44.2
	7 × 10 <sup>-6</sup>	531	43.6	63.8	160.2	0.530	53.0
	9 × 10 <sup>-6</sup>	270	38.1	108.4	454.2	0.589	58.9
	11 × 10 <sup>-6</sup>	257	34.9	83.5	190.1	0.623	62.3

utilizing Equation (1):

$$\%IE_p = \left[ \frac{i_{Corr}^{\circ} - i_{Corr}}{i_{Corr}^{\circ}} \right] \times 100 \quad (1)$$

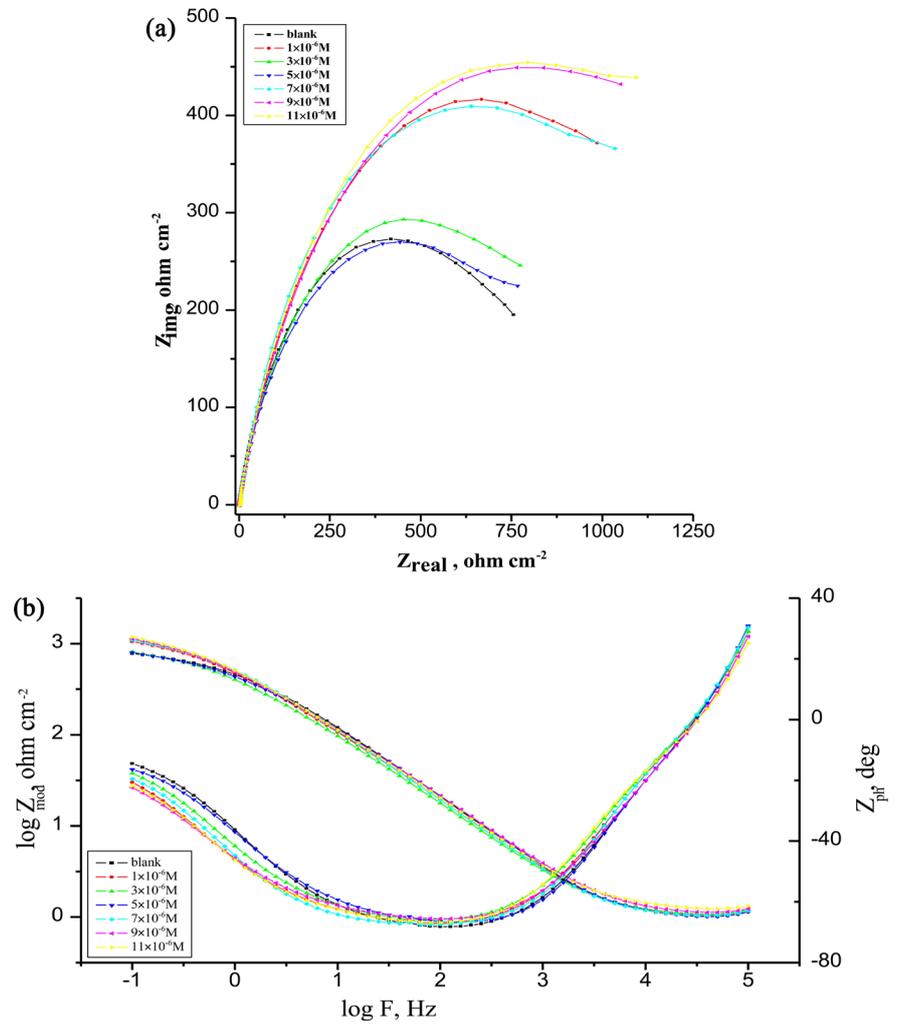
where  $i_{Corr}^{\circ}$  and  $i_{Corr}$  are the uninhibited and inhibited corrosion current densities, correspondingly.

Also it is clear from **Table 3** that ( $\beta_a$ ) and ( $\beta_c$ ) Tafel lines keep almost unmoved upon appending of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile composite, mean rise to nearly parallel set of anodic lines slope, and nearly parallel cathodic diagrams data gotten too. Therefore, the inhibitors adsorbed play by simple blocking of the active center for two anodic and cathodic procedures. Meaning no change in mechanism of Cu in solution, and only reasons inactivation of a part of the surface with esteem to the aggressive solution [31] [32].

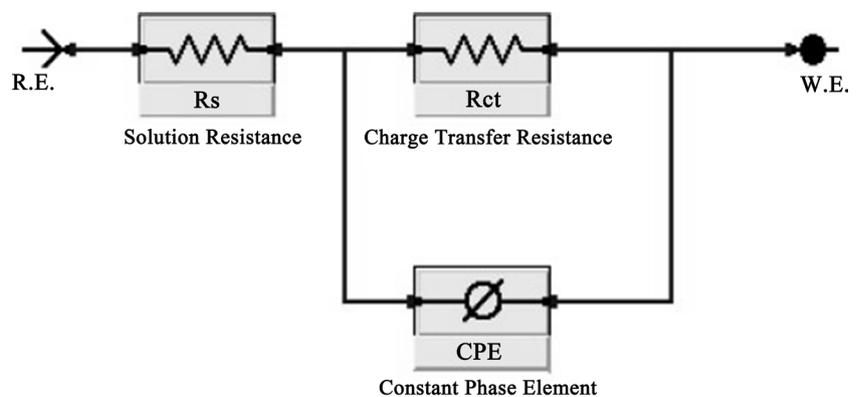
### 3.2. EIS Tests

EIS is well-established and commanding tests in the reading of corrosion. Surface characteristic and mechanistic data can be gotten from impedance diagrams [33] [34] [35] [36] [37]. **Figure 2(a)** & **Figure 2(b)** display the Nyquist (a) and Bode (b) diagrams gotten at OCP both in the attendance and lack of improving dose of examined 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile compound at 30 °C ± 0.1 °C. The improve in the size of the capacitive loop with the appending of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile composite at 30 °C ± 0.1 °C displays that a barrier progressively forms on the surface of Cu. Bode schemes (see **Figure 2(b)**), displays the incessant rise in the phase angle shift, clearly correlating with the rise of adsorbed inhibitor on surface of Cu. The Nyquist schemes do not produce perfect semicircles as predictable from the theory of EIS. The abnormality from ideal semicircle was usually credited to the frequency scattering [38] as well as to the in-homogeneities of the surface.

EIS data of the 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile campsite at 30 °C ± 0.1 °C was examine utilize the equivalent circuit (**Figure 3**), which signifies a single charge transfer reaction and



**Figure 2.** The Nyquist (a) and Bode (b) diagrams for Cu corrosion in nonexistence and existence of unlike dose of 2-amino-6-methyl-5-oxo-4-phenyl-5, 6-dihydro-4H-pyrano [3,2-c]quinoline-3-carbonitrile composite at  $30^\circ\text{C} \pm 0.1^\circ\text{C}$ .



**Figure 3.** Equivalent circuit model utilized to fit investigational EIS.

fits well with our experimental data. The constant phase element, CPE, is presented in the circuit in its place of a pure double layer capacitor to give a more correct fit [39]. The double layer capacitance,  $C_{dl}$ , for a circuit including

$$C_{dl} = Y_o \omega^{n-1} / \sin[n(\pi/2)] \quad (2)$$

where  $Y_o$  is the degree of the CPE,  $\omega = 2\pi f_{\max}$ ,  $f_{\max}$  is the frequency at the impedance is maximal and the factor  $n$  is an parameter adjustable that regularly lies among 0.50 and 1.0 [40] [41] [42]. The overall figure of the plots is very like for all samples (in existence and nonexistence of inhibitor at unlike immersion times) representing that no exchange in the corrosion mechanism [43]. From the impedance data (see Table 4), we achieve that the data of  $R_{ct}$  improves with rising the dose of the inhibitor and this designates an improvement in %IE, which in agreement with the data gotten from Potentiodynamic polarization.

In fact, the existence of inhibitor improves the data of  $R_{ct}$  in acidic solution. Data of  $C_{dl}$  are also brought down to the extreme extent in the existence of inhibitor and the break down in the data of CPE trails the order like to that gotten for  $i_{Corr}$  in this study. The lower  $C_{PE}/C_{dl}$  data from a break down in local dielectric constant and/or an improvement in the width of the double layer, signify that organic assembles hinder the Cu corrosion by metal/acid adsorbed [44] [45]. The %IE was measured from the charge transfer resistance data from Equation (3) [46]:

$$\%IE_{EIS} = \left[1 - \left(R_{ct}^{\circ} / R_{ct}\right)\right] \times 100 \quad (3)$$

where  $R_{ct}^{\circ}$  and  $R_{ct}$  are the resistance data nonexistence and existence of inhibitor correspondingly.

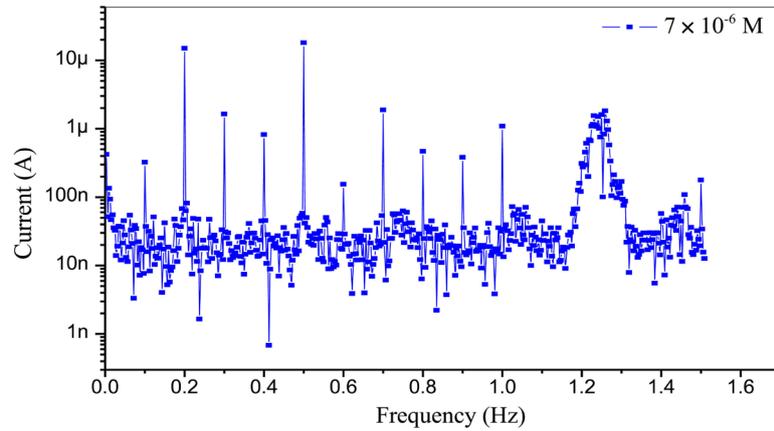
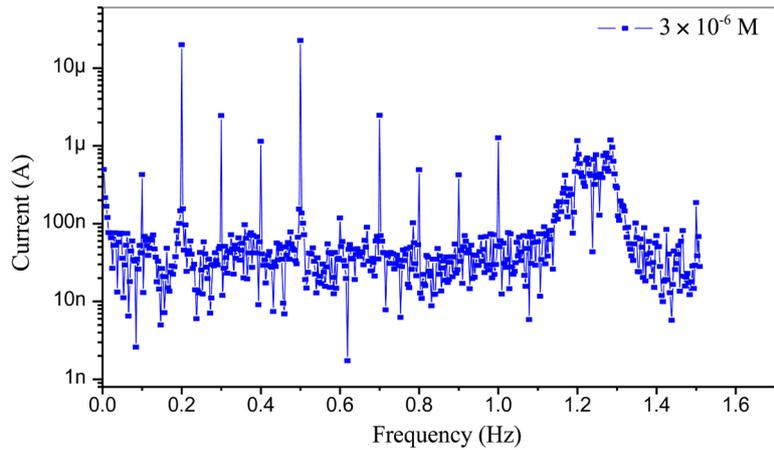
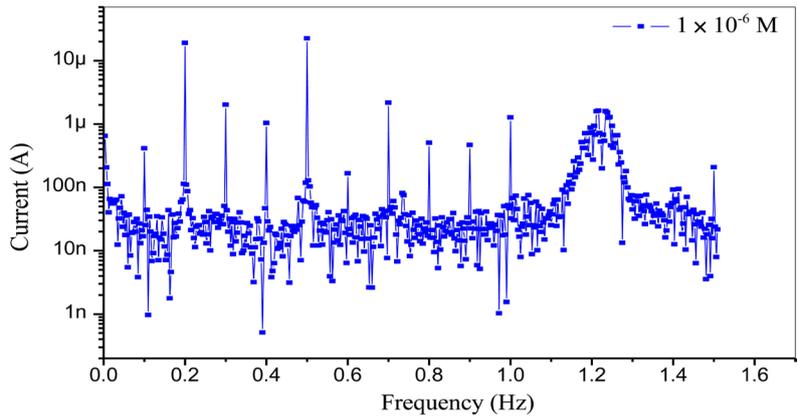
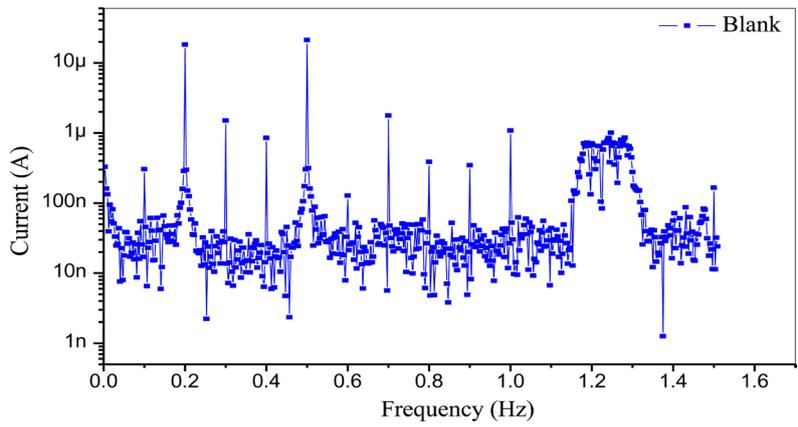
### 3.3. EFM Tests

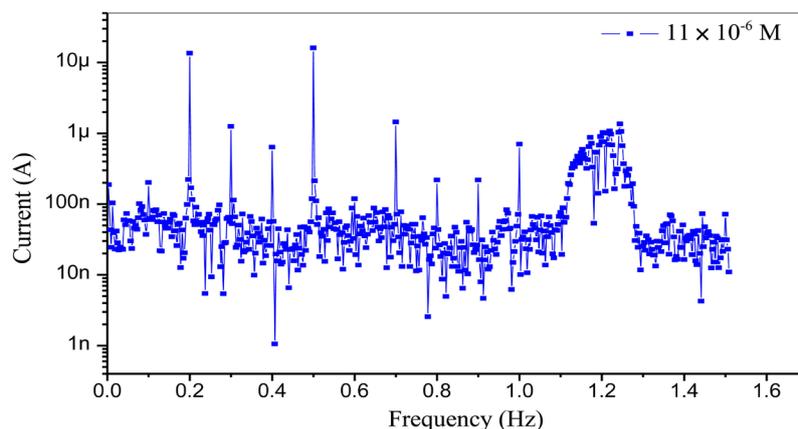
EFM is a no damaging corrosion tests that can straight and quickly measure the corrosion current data without prior information of Tafel slopes, and with only a lesser polarizing signal. These benefits of EFM test make it an ideal applicant for online corrosion observing [47]. The higher strength of the EFM is the causality factors which attend as an inner check on the power of EFM calculation.

Figure 4 displays the EFM of Cu in nitric acid solution inclosing altered dose of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-

**Table 4.** Outcome data gotten from EIS test for Cu in 2 M HNO<sub>3</sub> in the nonexistence and existence of unlike dose of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile compound at 30°C ± 0.1°C.

Compound	Conc. (M)	$R_s \times 10^{-3}$ $\Omega \cdot \text{cm}^2$	$Y_o \times 10^{-6}$ $\mu\Omega^{-1} \cdot \text{s}^n$	$n \times 10^{-3}$	$R_{ct}$ $\Omega \cdot \text{cm}^2$	$C_{dl} \times 10^{-4}$ $\mu\text{F} \cdot \text{cm}^{-2}$	$\theta$	%IE <sub>EIS</sub>
	Blank	0.995	291.0	800.4	751.6	9.0	-----	-----
	$1 \times 10^{-6}$	0.942	320.1	786.3	799.2	7.8	0.059	5.9
2-amino-6-methyl-5-oxo-4-phenyl- 5,6-dihydro-4H-pyrano[3,2-c]quinoline- 3-carbonitrile	$3 \times 10^{-6}$	1.017	404.2	776.8	828.2	7.7	0.092	9.2
	$5 \times 10^{-6}$	0.993	365.7	780.7	1003.7	7.6	0.251	25.1
	$7 \times 10^{-6}$	0.979	329.3	794.5	1228.3	7.5	0.388	38.8
	$9 \times 10^{-6}$	1.044	366.0	765.0	1320.2	7.2	0.430	43.0
	$11 \times 10^{-6}$	1.175	351.0	778.7	1550.2	6.8	0.515	51.1





**Figure 4.** EFM data for Cu nonexistence and existence of different dose of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile composite at  $30^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ .

3-carbonitrile compound at  $30^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ . The harmonic and intermodulation peaks are obviously visible and are much greater than the background noise. The investigational EFM value was preserved utilized two unlike models: complete dispersion control of the cathodic reaction and the “activation” model. For the second, a set of three non-linear equations had been explained, pretentious that the corrosion potential does not exchange due to the polarization of the electrode working [48]. The greater signal was utilized to measure  $i_{corr}$ , ( $\beta_C$  and  $\beta_a$ ) and (CF-2 and CF-3). These parameters gotten from EFM were recorded in **Table 5**. The data demonstration that, the appending of tested composite at unlike doses to the acidic solution lower  $i_{corr}$ , signifying that this composite hinder the corrosion of Cu concluded adsorption. The CF gotten under altered experimental conditions are nearly equal to the values gotten from theoretical Equations (2) and (3) representing that the calculated data are confirmed and best quality.  $\%IE_{EFM}$  was improved by improving the inhibitor dose and was measured as from Equation (4):

$$IE_{EFM} = \left[ 1 - \left( i_{Corr} / i_{Corr}^{\circ} \right) \right] \times 100 \quad (4)$$

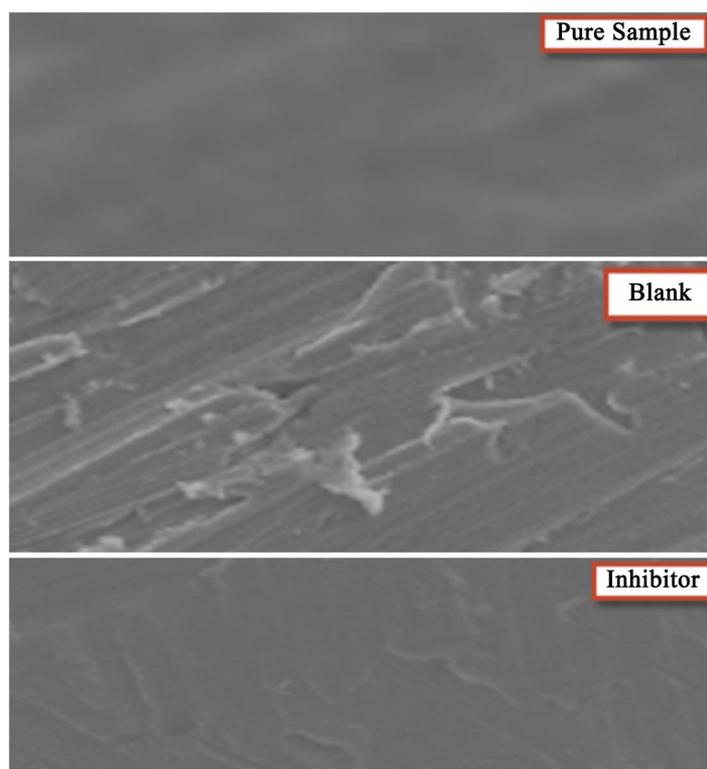
where  $i_{Corr}^{\circ}$  and  $i_{Corr}$  are current nonexistence and existence of inhibitor, correspondingly.

### 3.4. SEM Examination and EDX Analysis

The creation of a defending surface film of inhibitor at the electrode surface was further established by SEM clarifications of the Cu surface. Also, in order to see whether the organic additive is adsorbed on the Cu surface or not, both SEM and EDX tests were occurred. **Figure 5** displays the SEM of fresh Cu surface nonexistence any appending of acid or the inhibitor. The images for Cu surface unprotected to 2.0 M  $\text{HNO}_3$  solution nonexistence and existence the appending of the optimum dose of the 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile composites are exposed in **Figure 5**. As

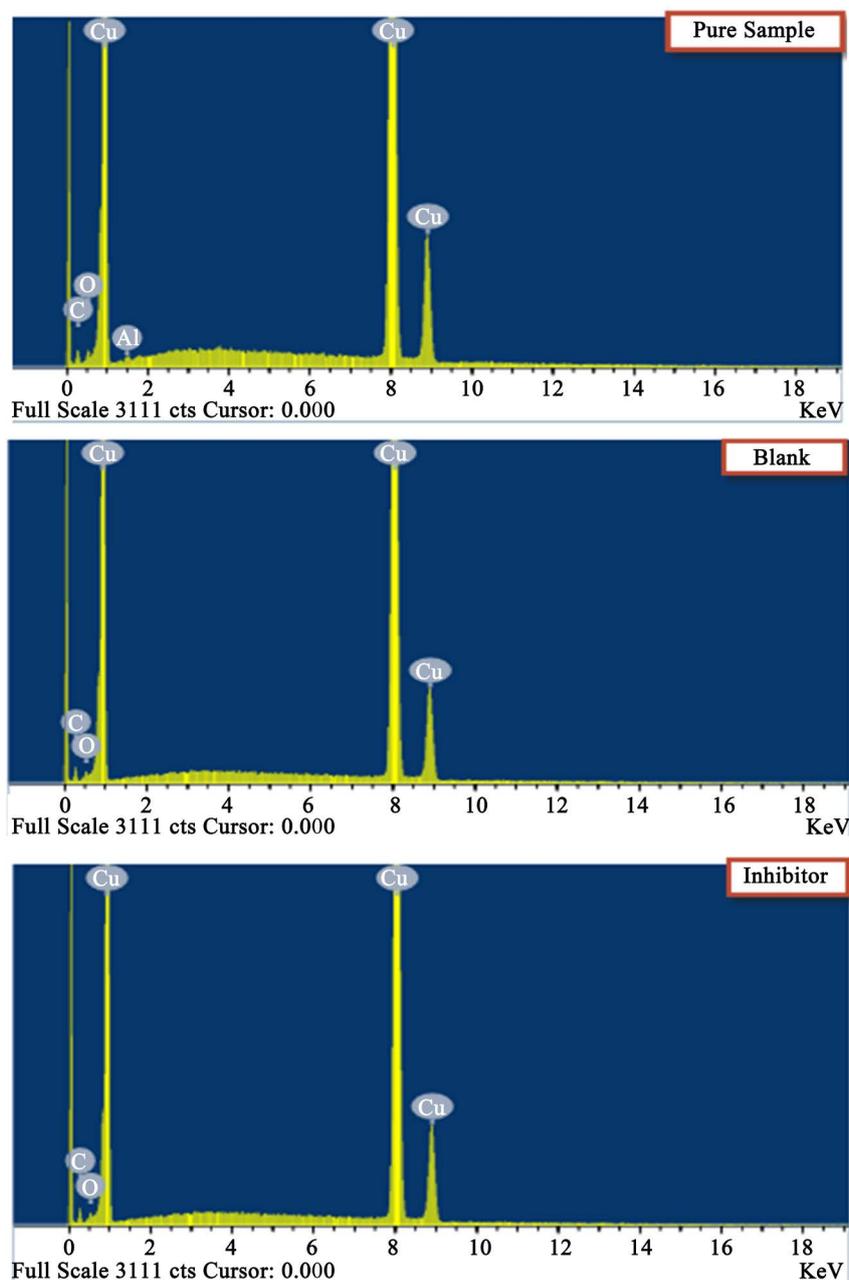
**Table 5.** Outcome data gotten from EFM test for Cu in 2 M HNO<sub>3</sub> in the a in nonexistence and existence of unlike dose of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile at 30°C ± 0.1°C.

Inhibitor	Conc. (M)	$i_{corr}$ ( $\mu\text{A}\cdot\text{cm}^{-2}$ )	$\beta_a \times 10^{-3}$ ( $\text{mV}\cdot\text{dec}^{-1}$ )	$\beta_c \times 10^{-3}$ ( $\text{mV}\cdot\text{dec}^{-1}$ )	CF-2	CF-3	$\theta$	% $IE_{EFM}$
	Blank	39.66	69.0	104.5	1.98	2.94	-----	-----
	$1 \times 10^{-6}$	23.62	63.9	104.2	1.99	2.94	0.404	40.4
2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile	$3 \times 10^{-6}$	22.44	58.3	99.7	2.03	3.11	0.434	43.4
	$5 \times 10^{-6}$	20.21	78.1	118.3	1.96	2.91	0.490	49.0
	$7 \times 10^{-6}$	19.23	66.9	119.8	1.94	2.85	0.515	51.5
	$9 \times 10^{-6}$	11.32	73.9	131.2	1.89	2.91	0.714	71.4
	$11 \times 10^{-6}$	9.54	65.6	104.7	2.01	3.01	0.759	75.9

**Figure 5.** SEM images of Cu in 2.0 M HNO<sub>3</sub> solution after inundation for 3 days non-existence inhibitor and in existence of  $11 \times 10^{-6}$  M of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile.

can be gotten, there was a noticeable perfection in the surface image of Cu that was preserved with the inhibitor due to the creation of an adsorbed protecting film of the inhibitor at the Cu surface.

The EDX profile examination exists in **Figure 6**. The EDX review spectra were utilized to measure which elements of inhibitor existed on the electrode surface earlier and later contact to the inhibitor solution. For the coins' nonexistence inhibitor behavior (**Figure 6**), only Cu was noticed. This is established by utilizing XRD, the chief corrosion yields designed on exposed Cu to nitric acid were



**Figure 6.** EDS images of Cu in 2.0 M HNO<sub>3</sub> solution after inundation for 3 days nonexistence inhibitor and in existence of  $11 \times 10^{-6}$  M of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile.

recognized as the basic Cu nitrate, gerhardtite ( $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$ ) and to a slighter amount cuprite ( $\text{Cu}_2\text{O}$ ) [49] [50]. It is observed the existence of the C, O and N signal in the EDX spectra in the example of the coins showing to the inhibitor, could be qualified to the adsorption of organic moiety at the surface of Cu. The rise in quantity of C atom in the item of assemblies (15.73%), specified that the liquefaction of Cu is very hinder by composite and thus shows a very high hinder capacity. Also, a strong enrichment with C is renowned in the example of campsite (see **Table 6**). The EDX of **Figure 6** display that the O is significantly

**Table 6.** Element gotten from EDX of copper in 2.0 M HNO<sub>3</sub> solution after inundation for days nonexistence of inhibitor and in existence of  $11 \times 10^{-6}$  M of 2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile.

Weight %	C	O	Al	Cu
Pure Sample	9.24	1.87	0.45	88.44
Blank	12.13	3.52	----	84.35
Inhibitor	15.73	2.45	----	81.82

suppressed relative to the coins ready in 2.0 M HNO<sub>3</sub> solution, and definitely this suppression will improve with improve examined dose and engagement time. The destruction of the O occurred due to the overlying inhibitor film. Also it is significant to notification the quantity of Cu peaks of EDX spectra is rise in the existence of inhibitor in a contrast of EDX analysis gotten in the nonexistence of inhibitor might representative that the examined molecule defensive the Cu surface in contradiction of acid corrosion. The configuration of the distinguished elements on the surface of Cu designates that the inhibitor molecule is powerfully adsorbed on the Cu creating a Cu-examined molecule bond, thus hinder the surface against corrosion.

### 3.5. Mechanism of Inhibition

Protection of the corrosion of Cu in 2.0 M HNO<sub>3</sub> solution by examined composite is measured by PP measurements, EIS, EFM and SEM studies; it was obtained that the protection efficiency relies on dose, metal nature, the manner of adsorption of the inhibitors and surface environments.

The corrosion hindrance is due to the inhibitors have adsorbed at the interface of solution/electrode, the amount of adsorption of an inhibitor rely on the type of the metal, the adsorption mode of the inhibitor and the conditions of surface. Adsorption on Cu surface is expected occurred mostly among the active site involved in the inhibitor and would rely on their charge density. The lone pairs of electrons transfer on the N atoms to the Cu surface to procedure a coordinate kind of linkage is favored by the existence of a vacant orbital in Cu atom of little energy.

It was decided that the kind of adsorption rely on the attraction of the Cu to the clouds  $\pi$ -electron of the ring structure. Metals for example Cu, which have a better affinity near aromatic moieties, were gotten to adsorb benzene rings in orientation flat.

2-amino-6-methyl-5-oxo-4-phenyl-5,6-dihydro-4H-pyrano[3,2-c]quinoline-3-carbonitrile assembled displays best hindrance power due to: i) the attendance of CH<sub>3</sub> group which is an electron giving group, also this CH<sub>3</sub> will improve the electron charge density on the structure, ii) its bigger size of molecular weight (329.25) that may simplify enhanced surface coating, and iii) its adsorption among five active site.

### 3.6. Conclusions

- 1) The analysis details of composite reveal that, it is an excellent corrosion hindrance for Cu in 2.0 M HNO<sub>3</sub>.
- 2)  $C_{dl}$  breaks down with respect to the blank solution when adding inhibitor. This fact may be decided by inhibitor molecule adsorbed on the surface of Cu.
- 3) EFM can be utilized for calculation of corrosion in a lack of prior data of Tafel lines slope.
- 4) The morphology of Cu existence and nonexistence was observed by (SEM) and (EDX).

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

### References

- [1] Khaled, K.F., Fadl-Allah, A.S. and Hammouti, B. (2009) Some Benzotriazole Derivatives as Corrosion Inhibitors for Copper in Acidic Medium: Experimental and Quantum Chemical Molecular Dynamics Approach. *Materials Chemistry and Physics*, **117**, 148-155. <https://doi.org/10.1016/j.matchemphys.2009.05.043>
- [2] AbdEl-Maksoud, S.A. (2004) Some Phthalazin Derivatives as Non Toxic Corrosion Inhibitors for Copper in Sulphuric Acid. *Electrochimica Acta*, **49**, 4205-4212. <https://doi.org/10.1016/j.electacta.2004.04.015>
- [3] Zarrouk, A., Hammouti, B. and Dafali, A. (2014) A Theoretical Study on the Inhibition Efficiencies of Some Quinoxalines as Corrosion Inhibitors of Copper in Nitric Acid. *Journal of Saudi Chemical Society*, **18**, 450-455. <https://doi.org/10.1016/j.jscs.2011.09.011>
- [4] El-Naggar, M.M. (2000) Is-Aminoazoles Corrosion Inhibitors for Copper in 4.0 M HNO<sub>3</sub> Solutions. *Corrosion Science*, **42**, 773-784. [https://doi.org/10.1016/S0010-938X\(99\)00066-9](https://doi.org/10.1016/S0010-938X(99)00066-9)
- [5] Treacy, G.M., Wilcox, G.D. and Richardson, M.O.W. (1999) Behaviour of Molybdate-Passivated Zinc Coated Steel Exposed to Corrosive Chloride Environments. *Journal of Applied Electrochemistry*, **29**, 647-654. <https://doi.org/10.1023/A:1026461924663>
- [6] Elmorsi, M.A. and Hassanein, A.M. (1999) Corrosion Inhibition of Copper by Heterocyclic Science. *Corrosion Science*, **41**, 2337-2352. [https://doi.org/10.1016/S0010-938X\(99\)00061-X](https://doi.org/10.1016/S0010-938X(99)00061-X)
- [7] Abd El-Maksoud, S.A. and Hassan, H.H. (2007) Electrochemical Studies on the Effect of (2E)-3-amino-2-phenylazo-but-2-enenitrile and Its Derivative on the Behavior of Copper in Nitric Acid. *Materials and Corrosion*, **58**, 369-375. <https://doi.org/10.1002/maco.200604021>
- [8] Khaled, K.F. (2008) Guanidine Derivative as a New Corrosion Inhibitor for Copper in 3% NaCl Solution. *Materials Chemistry and Physics*, **112**, 104-111. <https://doi.org/10.1016/j.matchemphys.2008.05.052>
- [9] El-Kot, A.M. and AL-Suhybani, A.A. (2013) Organic and Inorganic Corrosion Inhibitors for Copper in HNO<sub>3</sub> Studied by Two Methods. *British Corrosion Journal*, **22**, 29-31. <https://doi.org/10.1179/000705987798271848>

- [10] Assaf, F.H., Krishna, M.A. and Kodari, M. (2003) Studies on Dissolution and Inhibition of Copper in Nitric Acid Using Stripping Voltammetry and Conductance Measurement. *Materials Chemistry and Physics*, **77**, 192-203. [https://doi.org/10.1016/S0254-0584\(01\)00597-1](https://doi.org/10.1016/S0254-0584(01)00597-1)
- [11] Herrag, L., Bourlah, M. and Patel, N.S. (2012) Experimental and Theoretical Study for Corrosion Inhibition of Mild Steel 1 M HCl Solution by Some New Diaminopropanenitrile Compounds. *Research on Chemical Intermediates*, **38**, 1669-1690. <https://doi.org/10.1007/s11164-012-0493-1>
- [12] Al-Kharafi, F.M., Abdullah, A.M. and Ateya, B.G. (2007) Effect of Sulfide Pollution on the Stability of the Protective Film of Benzotriazole on Copper. *Applied Surface Science*, **253**, 8986-8991. <https://doi.org/10.1016/j.apsusc.2007.05.017>
- [13] Ramji, K., Cairns, D.R. and Rajeswari, S. (2008) Synergistic Inhibition Effect of 2-Mercaptobenzothiazole and Tween-80 on the Corrosion of Brass in NaCl Solution. *Applied Surface Science*, **254**, 4483-4493. <https://doi.org/10.1016/j.apsusc.2008.01.031>
- [14] Altaf, F., Qureshi, R. and Ahmed, S. (2010) Electrochemical Adsorption Studies of Urea on Copper Surface in Alkaline Medium. *Journal of Electroanalytical Chemistry*, **642**, 98-101. <https://doi.org/10.1016/j.jelechem.2010.02.011>
- [15] Varvara, S., Muresan, L.M., Rahmouni, K. and Takenouti, H. (2008) Evaluation of Some Non-Toxic Thiadiazole Derivatives as Bronze Corrosion Inhibitors in Aqueous Solution. *Corrosion Science*, **50**, 2596-2604. <https://doi.org/10.1016/j.corsci.2008.06.046>
- [16] Lashgari, M., Arshadi, M.R. and Biglar, M. (2010) Experimental and Theoretical Studies of Media Effects on Copper Corrosion in Acidic Environments Containing 2-amino-5-mercapto-1,3,4-thiadiazole. *Journal of the Iranian Chemical Society*, **7**, 478-486. <https://doi.org/10.1007/BF03246035>
- [17] Easton, E. and Pickup, P.G. (2005) An Electrochemical Impedance Spectroscopy Study of Fuel Cell Electrodes. *Electrochimica Acta*, **50**, 2469-2474. <https://doi.org/10.1016/j.electacta.2004.10.074>
- [18] Krishnaveni, K. and Ravichandran, J. (2014) Influence of Aqueous Extract of Leaves of *Morinda tinctoria* on Copper Corrosion in HCl Medium. *Journal of Electroanalytical Chemistry*, **735**, 24-31. <https://doi.org/10.1016/j.jelechem.2014.09.032>
- [19] Sherif, E.M., Erasmus, R.M. and Comins, G.D. (2010) *In Situ* Raman Spectroscopy and Electrochemical Techniques for Studying Corrosion and Corrosion Inhibition of Iron in Sodium Chloride Solutions. *Electrochimica Acta*, **55**, 3657-3663. <https://doi.org/10.1016/j.electacta.2010.01.117>
- [20] Fouda, A.S. and Abdul Wahed, H.A. (2016) Corrosion Inhibition of Copper in HNO<sub>3</sub> Solution Using Thiophene and Its Derivatives. *Arabian Journal of Chemistry*, **9**, 91-99. <https://doi.org/10.1016/j.arabjc.2011.02.014>
- [21] Khadom, A.A., Yaro, A.S. and Kadum, A.A.H. (2010) Corrosion Inhibition by Naphthylamine and Phenylenediamine for the Corrosion of Copper-Nickel Alloy in Hydrochloric Acid. *Journal of the Taiwan Institute of Chemical Engineers*, **41**, 122-125. <https://doi.org/10.1016/j.jtice.2009.08.001>
- [22] Tang, Y., Yang, X., Yang, W. and Wan, R. (2010) Experimental and Molecular Dynamics Studies on Corrosion Inhibition of Mild Steel by 2-amino-5-phenyl-1,3,4-thiadiazole. *Corrosion Science*, **52**, 242-249. <https://doi.org/10.1016/j.corsci.2009.09.010>
- [23] Rajeswari, V. and Devarayam, K. (2017) Expired Pharmaceutical Compounds as Potential Inhibitors for Cast Iron Corrosion in Acidic Medium. *Research on Chem-*

- ical Intermediates*, **43**, 3893-3913. <https://doi.org/10.1007/s11164-016-2852-9>
- [24] Maddila, S., Rana, S. and Johalagadda, S.B. (2015) Synthesis of Pyrazole-4-Carbonitrile Derivatives in Aqueous Media with CuO/ZrO<sub>2</sub> as Recyclable Catalyst. *Catalysis Communications*, **61**, 26-30. <https://doi.org/10.1016/j.catcom.2014.12.005>
- [25] Rauf, A., Bogaerts, W.F. and Mahdi, E. (2012) Implementation of Electrochemical Frequency Modulation to Analyze Stress Corrosion Cracking. *Corrosion Science and Engineering*, **68**, 2-9. <https://doi.org/10.5006/1.3691836>
- [26] Abdel-Rehim, S.S., Khaled, K.F. and Abd-Elshafi, N.S. (2006) Electrochemical Frequency Modulation as a New Technique for Monitoring Corrosion Inhibition of Iron in Acid Media by New Thiourea Derivative. *Electrochimica Acta*, **51**, 3269-3277. <https://doi.org/10.1016/j.electacta.2005.09.018>
- [27] Quartarone, G., Moretti, G., Bellomi, T., Capobianco, G. and Zingales, A. (2003) Inhibition of Copper Corrosion by Isatin in Aerated 0.5 M H<sub>2</sub>SO<sub>4</sub>. *Corrosion Science*, **45**, 715-733. [https://doi.org/10.1016/S0010-938X\(02\)00134-8](https://doi.org/10.1016/S0010-938X(02)00134-8)
- [28] Bjomdahl, W.D. and Nobe, K. (1984) Copper Corrosion in Chloride Media. Effect of Oxygen. *Corrosion Science and Engineering*, **40**, 82-87. <https://doi.org/10.5006/1.3593920>
- [29] Zelinsky, A.G., Pirogov, B.Y. and Yurjev, O.A. (2004) Open Circuit Potential Transients and Electrochemical Quartz Crystal Microgravimetry Measurements of Dissolution of Copper in Acidic Sulfate Solutions. *Corrosion Science*, **46**, 1083-1093. <https://doi.org/10.1016/j.corsci.2003.09.008>
- [30] Amin, M.A. (2006) Weight Loss, Polarization, Electrochemical Impedance Spectroscopy, SEM and EDX Studies of the Corrosion Inhibition of Copper in Aerated NaCl Solutions. *Journal of Applied Electrochemistry*, **36**, 215-226. <https://doi.org/10.1007/s10800-005-9055-1>
- [31] Khaled, K.F. (2008) Adsorption and Inhibitive Properties of a New Synthesized Guanidine Derivative on Corrosion of Copper in 0.5 M H<sub>2</sub>SO<sub>4</sub>. *Applied Surface Science*, **255**, 1811-1818. <https://doi.org/10.1016/j.apsusc.2008.06.030>
- [32] Gadallah, A.G., Badway, M.W., Rehan, H.H. and Abu-Romia, M.M. (1989) Inhibition of Corrosion of  $\alpha$ -Brass (Cu-Zn, 67/33) in Acid Chloride Solutions by Some Amino Pyrazole Derivatives. *Journal of Applied Electrochemistry*, **19**, 928-932. <https://doi.org/10.1007/BF01007942>
- [33] Cheng, T.P. and Tung, J. (1990) Corrosion of Reinforcements in Artificial Sea Water and Concentrated Sulfate Solution. *Cement and Concrete Research*, **20**, 243-252. [https://doi.org/10.1016/0008-8846\(90\)90077-B](https://doi.org/10.1016/0008-8846(90)90077-B)
- [34] Kendling, M.W., Mansfeld, F. and Lindberg, G. (1983) A Computer Analysis of Electrochemical Impedance Data. *Corrosion Science*, **23**, 1007-1015. [https://doi.org/10.1016/0010-938X\(83\)90027-6](https://doi.org/10.1016/0010-938X(83)90027-6)
- [35] Milocco, R.H. (1989) An Iterative Least Squares Method for the Identification of Electrochemical Impedances. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **24**, 243-255. [https://doi.org/10.1016/0022-0728\(89\)87017-2](https://doi.org/10.1016/0022-0728(89)87017-2)
- [36] Debuxck, F., Emaitre, L. and Weyten, L. (1988) Estimating the Barrier Layer Thickness of Porous Aluminium Oxide Films with A.C. Impedance Measurements. *Surface and Coatings Technology*, **34**, 311-318. [https://doi.org/10.1016/0257-8972\(88\)90121-1](https://doi.org/10.1016/0257-8972(88)90121-1)
- [37] Kapusta, S. and Hackerman, N. (1982) The Electroreduction of Formaldehyde on Tin and Indium. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, **138**, 295-313. [https://doi.org/10.1016/0022-0728\(82\)85084-5](https://doi.org/10.1016/0022-0728(82)85084-5)

- [38] Kuruvilla, M., John, S. and Joseph, A. (2013) Electrochemical Studies on the Interaction of L-cysteine with Metallic Copper in Sulfuric Acid. *Research on Chemical Intermediates*, **39**, 3513-3543. <https://doi.org/10.1007/s11164-012-0860-y>
- [39] Macdonald, J.R., Johanson, W.B. and Macdonald, J.R. (1987) Theory in Impedance Spectroscopy. John Wiley & Sons, New York.
- [40] Sorkhabi, A.A. and Jeddi, N.G. (2005) Inhibition Effect of Polyethylene Glycol on the Corrosion of Carbon Steel in Sulphuric Acid. *Materials Chemistry and Physics*, **92**, 480-486. <https://doi.org/10.1016/j.matchemphys.2005.01.059>
- [41] TrabANELLI, G., Montecelli, C., Grassi, V. and Frignani, A. (2005) Electrochemical Study on Inhibitors of Rebar Corrosion in Carbonated Concrete. *Cement and Concrete Research*, **35**, 1804-1813. <https://doi.org/10.1016/j.cemconres.2004.12.010>
- [42] Fouda, A.S., Ibrahim, H. and Atef, M. (2017) Adsorption and Inhibitive Properties of Sildenafil (Viagra) for Zinc in Hydrochloric Acid Solution. *Results in Physics*, **7**, 3408-3418. <https://doi.org/10.1016/j.rinp.2017.08.012>
- [43] Rosliza, R. and Senin, H.B. (2008) The Effect of Inhibitor on the Corrosion of Aluminum Alloys in Acidic Solution. *Materials Chemistry and Physics*, **107**, 281-288. <https://doi.org/10.1016/j.matchemphys.2007.07.013>
- [44] Lagrenee, M., Mernari, B., Bouanis, M.T., Traisnel, M. and Bentiss, F. (2002) Study of the Mechanism and Inhibiting Efficiency of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole on Mild Steel Corrosion in Acidic Media. *Corrosion Science*, **44**, 573-588. [https://doi.org/10.1016/S0010-938X\(01\)00075-0](https://doi.org/10.1016/S0010-938X(01)00075-0)
- [45] McCafferty, E. (2005) Validation of Corrosion Rates Measured by the Tafel Extrapolation Method. *Corrosion Science*, **47**, 3202-3215. <https://doi.org/10.1016/j.corsci.2005.05.046>
- [46] Wang, C.T., Chen, S.H. and Ma, H.Y. (2003) Protection of Copper Corrosion by Carbazole and N-Vinylcarbazole Self-Assembled Films in NaCl Solution. *Journal of Applied Electrochemistry*, **33**, 179-1862. <https://doi.org/10.1023/A:1024097208128>
- [47] Khaled, K.F. (2008) Application of Electrochemical Frequency Modulation for Monitoring Corrosion and Corrosion Inhibition of Iron by Some Indole Derivatives in Molar Hydrochloric Acid. *Materials Chemistry and Physics*, **112**, 290-300. <https://doi.org/10.1016/j.matchemphys.2008.05.056>
- [48] Eldesoky, A.M., Fouda, A.S. and Nabih, A. (2013) Inhibitive, Adsorption, Synergistic Studies on Copper Corrosion in Nitric Acid Solutions by Some Organic Derivatives. *Advances in Materials and Corrosion*, **2**, 1-15.
- [49] Walaa, A.H. and Gaber, G. (2016) Studies of Corrosion and Electrochemical Behavior of Cu-Zn Alloys in H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> Acid Solutions. *Metallurgical Engineering*, **5**, 27-37. <https://doi.org/10.14355/me.2016.05.003>
- [50] Tidblad, J., Kucera, V., Samie, F. and Das, S.N. (2007) Exposure Programme on Atmospheric Corrosion Effects of Acidifying Pollutants in Tropical and Subtropical Climates. *Water, Air, & Soil Pollution: Focus*, **7**, 241-247. <https://doi.org/10.1007/s11267-006-9078-6>