

Corrosion Inhibition of Copper in Acid Medium by Drugs: Experimental and Theoretical Approaches

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Abstract: The inhibition performances of nafcillin (III), methicillin (II) and penicillin G (I) on the corrosion of copper in HCl was studied and tested by weight loss, Tafel polarization, SEM, UV-vis spectrophotometry, molecular dynamics method and quantum chemical calculations. Polarization curves indicated that the studied inhibitors act as mixed-type inhibitors. The values of inhibition efficiency and surface coverage were found to follow the order: Blank < penicillin < methicillin < nafcillin. The maximum inhibition efficiency of 98.28% was exhibited by nafcillin, and the minimum inhibition efficiency of 43.10% was showed by penicillin. The adsorption of inhibitors obeys the Temkin adsorption isotherm. The negative value of free energy of adsorption ΔG_{ads} , indicated that the adsorption of three inhibitors was a spontaneous process. The SEM micrographs confirmed the protection of copper in a 1 M HCl solution by penicillin G, nafcillin, and methicillin. The shape of the UV/vis spectra of inhibitors in the presence of the immersion of Cu showed a strong support to the possibility of the chemisorbed layer formation on Cu surface by nafcillin (between nafcillin and Copper) and physisorption between penicillin and methicillin with copper. DFT calculations were performed to provide further insight into the inhibition efficiencies which were determined experimentally. Molecular dynamics (MD) simulations were applied to find the most stable configuration and adsorption energies of penicillin G, nafcillin and methicillin molecules on Cu (110) surface. The interaction energy followed the order: nafcillin (III) > methicillin (II) > penicillin G (I), which confirmed that nafcillin has the strongest interaction with the metal surface. The obtained results from experimental and theoretical methods were in reasonable agreement.

Keywords: Copper, Antibacterial Drugs, Corrosion, Inhibitor, SEM, Molecular Dynamic Simulations

1. INTRODUCTION

Copper is widely used in many industries as a conductor in electrical power lines, pipelines for domestic and industrial water utilities including sea water, heat conductors, heat exchangers, etc. In these industries, to restrain the corrosion and oxidation after several working cycles, chemical cleaning treatment by acid is used which results in severe corrosion during exposure to aggressive media. One of the most effective and economic approaches to avoid corrosive effect of this acid on the copper is the use of a corrosion inhibitor [1-4].

Widespread researches are made to find corrosion inhibitors which are less toxic, environmentally-friendly, ecologically acceptable, readily available, and relatively low-cost drugs are used as good inhibitors for metals in acidic solution [5].

Theoretical calculations have proven to be a powerful tool in studying the interactions

between the inhibitor molecules and the metal surfaces. Therefore, recently an increasing attention has been seen on the involvement of these theoretical approaches in corrosion studies [6-17].

The purpose of this investigation is the evaluation of the corrosion inhibition of penicillin G, nafcillin, methicillin for copper in an acidic medium using gravimetric measurement, potentiodynamic polarization and isotherm calculations. We have also studied both the quantum chemical calculations and MD simulation to confirm the experimental outcomes.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Three compounds of penicillin G (CID 5904), nafcillin (CID 8982), and methicillin (CID 6087)

were obtained from Sigma and used without any further purification. The metal specimens used in this study were cut into 20 mm × 20 mm × 1 mm dimensions. Before measurements the samples were polished using different grades of emery paper. The specimens were washed thoroughly with bi-distilled water. They were degreased and placed in an ultrasonic acetone bath for about 5 minutes to remove any possible residue from polishing, and subsequently dried with acetone.

2. 2. Instrumentation

Electrochemical test of Tafel linear polarization were performed with an SAMA 500 Electroanalyser (SAMA Research Center, Iran) controlled using a personal computer in a conventional three-electrode cell. The morphology of the corroded copper surface in the presence and absence of inhibitor molecules was examined by a Hitachi scanning electronic microscope model S4160 FE with an accelerating voltage of 20 kV. All the UV- Vis absorption spectra measurements were carried out in the 200- 600 nm region using a Cary UV-vis spectrophotometer model Bio-300 with a 10 mm light-path black quartz spectrophotometer cell.

2. 3. Weight Loss Measurement

The gravimetric study (weight loss method) is recognized to be the most widely used process for monitoring inhibition efficiency [18]. The reliability of the result offered by the gravimetric method is such that this technique forms the baseline method of measurement in many programs of corrosion monitoring [19].

For weight loss measurements, the cleaned copper sheet with dimension of 20 mm × 20 mm × 1 mm was weighed before and after immersion in an open beaker containing the test solution for a period of time up to 3 h. Before testing, all specimens were abraded with sandpapers from number 500 to 1000 grit, cleaned with double distilled water and absolute acetone, then dried in room condition and weighted accurately. After testing, each specimen was taken out and washed carefully in absolute acetone under ultrasound until the corrosion products on the surface of the

specimens were removed thoroughly. They were then dried in an oven at 70 °C for 30 min and weighed accurately after cooling to room temperature. The weight loss experiments were performed at 296, 305 and 315 ±1K in the known inhibitor and acid concentrations. The average weight loss (W) for identical experiments were taken and expressed in mg.cm⁻². The corrosion rate, A, in g.cm⁻².h⁻¹ was determined from the equation [20]

$$A = \frac{W}{(\text{area} \times \text{time})} \quad (1)$$

The inhibition efficiency (IE) was calculated using the following equation (2) [21]

$$IE (\%) = \left[\frac{(W_0 - W)}{W_0} \right] \times 100 \quad (2)$$

where W_0 and W were the weight loss of the copper sheet in the absence and presence of the inhibitor, respectively. The surface coverage (θ) of the inhibitor on the copper surface was expressed by the following equation (3) [22]:

$$\theta = \frac{IE (\%)}{100} \quad (3)$$

2. 4. Electrochemical Measurements (Experimental)

A square cut from the copper sheet with dimensions of 20 mm × 20 mm × 1 mm was used as the working electrode. A platinum electrode and a saturated calomel electrode (SCE) were employed as the counter and reference electrodes, respectively. All tests were performed four times at room temperature. Before the tests, the working electrode (Copper Square) was polished mechanically, washed with acetone, rinsed numerous times with distilled water and then dried at room condition. All measurements were carried out with freshly polished electrodes in deaerated test solution. The cathodic and anodic polarization curves were recorded at a sweep rate of 50 mV.s⁻¹. To obtain the corrosion

current densities, the linear Tafel segments of the cathodic and anodic curves were extrapolated to the potential of corrosion.

The corrosion rate in different test solutions was determined using the Stern–Geary equation from the polarization measurement [23]:

$$J_{cor} = \frac{\beta_a \times \beta_c}{2.303 \times R_p \times (\beta_a + \beta_c)} \quad (4)$$

Whereas J_{cor} was the current density of corrosion, R_p was the polarization resistance and β_c and β_a were the cathodic and anodic Tafel slopes that were considered 0.1 V.dec^{-1} in our measurements.

The polarization resistance can be measured on the basis of the following equation (5)[24]:

$$R_p = \frac{\Delta E}{\Delta J} = \frac{\partial E}{\partial J} \quad (5)$$

The corrosion rate (Rate_{cor}) can be obtain with following equation (6) [25]:

$$\text{Rate}_{cor} = \frac{3270 \times J_{cor} \times M}{D \times V} \quad (6)$$

With $3270=0.01 \times [1 \text{ year (in seconds) } / 96497.8]$ and $96497.8 = 1 \text{ Faraday in Coulombs}$. Rate_{cor} was the corrosion rate (mpy), J_{cor} was the current density of corrosion (A.cm^{-2}), V was the sample volume (cm^3), M and D were the weight ($= 55.85 \text{ g}$) for unit mole and density ($= 7.87 \text{ g.cm}^{-3}$) of sample, respectively.

Inhibition efficiency (IE %) values were calculated from J_{cor} as follows [26]:

$$IE(\%) = \frac{(J'_{cor} - J_{cor})}{J'_{cor}} \times 100 \quad (7)$$

Whereas J'_{cor} and J_{cor} were the current densities of corrosion in the absence and presence of mentioned inhibitor.

2. 5. Computational Studies

Quantum chemical calculations were performed for penicillin G, nafcillin and

methicillin as corrosion inhibitors using the density functional theory (DFT) method at the hybrid functional B3LYP level of theory with 6-311++G** basis set [27-29] by the Gaussian 03 series of programs [30]. All obtained structures were minima of potential energy surface (without image frequency).

Reactive sites of the molecule can be determined by accounting three influencing factors: distribution of frontier molecular orbital, natural atomic charge and Fukui functions [31].

Local quantities such as Fukui function were considered in order to know which site in a molecule, in a considered reaction, is more reactive than others.

With respect to a finite difference approximation, the condensed Fukui functions were calculated as an atom k in a molecule with N electrons [32]:

$$F^+(r) = q_k(N) - q_k(N+1) \text{ For nucleophilic attack} \quad (8)$$

$$F^-(r) = q_k(N-1) - q_k(N) \text{ For electrophilic attack} \quad (9)$$

where $q_k(N)$, $q_k(N+1)$, and $q_k(N-1)$ were the charges of the k th atom for N , $N+1$, and $N-1$ electron systems, respectively. The preferred sites for the electrophilic and nucleophilic attacks were the atoms or the regions where values of $F^-(r)$ and $F^+(r)$ were maximum.

Molecular dynamics simulation (MD simulation) is a technique which is popular in studies of interaction between inhibitors and concerned metal surfaces. The interaction between an inhibitor and copper (Cu) surface was investigated by MD simulation using the Forcite module of the Materials Studio 6.0 software developed by Accelrys Inc [33]. The interaction between Cu (110) surface and inhibitor molecules was carried out in a simulation box ($72.294 \times 51.119 \times 78.195 \text{ \AA}$) with periodic boundary conditions. A vacuum slab of 50 \AA height was kept over the Cu (110) surface. Non-bonding, Vander Waals and electrostatic interactions were set as atom-based summations using the Ewald summation method with a cutoff radius of 15.50 \AA . Using twenty layers of copper atoms gives a sufficient depth that the inhibitor molecules will only be involved in non-bond

interactions with copper atoms in the layers of the surface, without unreasonably increasing the calculation time. During the simulation process two layers near in the Cu (110) surface were frozen and inhibitors were allowed to interact with the metal surface freely. The force field used was COMPASS (condensed phase optimized molecular potentials for atomistic simulation studies) force field. To construct a more reliable system, both water and hydrogen chloride molecules were added to the solution layer in the simulated system. The liquid phase consisted of 400 H₂O molecules, 5Cl⁻ ions, 5 H₃O⁺ ions and a single dissolved inhibitor molecule.

The MD simulation was performed at 298.0K under canonical ensemble (NVT) using a time step of 1.0 fs and a simulation time of 50 ps. the geometry of the system was optimized such that the total energy of the system was at a local minimum with respect to potential energy. Then, the dynamic process was carried out until the entire system reached equilibrium, at which both the temperature and the energy of the system

were balanced.

The interaction energy between the metal and the inhibitor were calculated according to the following equation[33];

$$E_{int} = E_{(total)} - (E_{surface} + E_{inhibitor} + E_{solution}) \quad (10)$$

3. RESULTS AND DISCUSSIONS

3. 1. Potentiodynamic Polarization Measurements

Fig. 1 displays the potentiodynamic polarization (Tafel) curves of copper sheet in HCl solution in the absence and presence of different concentrations of antibacterial drugs as the inhibitors.

The relevant parameters are listed in Table 1 as corrosion potential (E_{cor}), polarization resistance (R_p), corrosion current density (j_{cor}), corrosion rate (mpy) and inhibition efficiency (IE), respectively.

Table 1. Polarization parameters and the corresponding inhibition efficiencies for copper sheet in HCl solution containing different concentrations of studied antibacterial drugs at 25°C.

Inhibitor	mM	E cor(V)	Rp(ohm)	Jcor×10 ⁻⁴ (A/cm ²)	Rate Corrosion (mpy)	%IE
Penicillin G	0.00	-0.22	28.75	7.56	97.31	-
	0.05	-0.20	30.56	7.11	91.56	5.95
	0.07	-0.20	33.88	6.42	82.57	15.08
	0.10	-0.21	38.89	5.59	71.94	26.06
	0.14	-0.22	42.93	5.06	65.17	33.07
Methicillin	0.00	-0.22	28.75	7.56	97.31	-
	0.05	-0.20	32.75	6.64	85.43	12.17
	0.07	-0.21	38.49	5.65	72.70	25.26
	0.10	-0.22	42.25	5.15	66.22	31.88
	0.14	-0.21	46.13	4.71	60.66	37.70
Nafcillin	0.00	-0.22	28.75	7.56	97.31	-
	0.05	-0.22	33.26	6.54	84.12	13.49
	0.07	-0.22	41.06	5.30	68.13	29.89
	0.10	-0.22	45.55	4.77	61.43	36.90
	0.14	-0.21	46.48	4.68	60.19	38.10

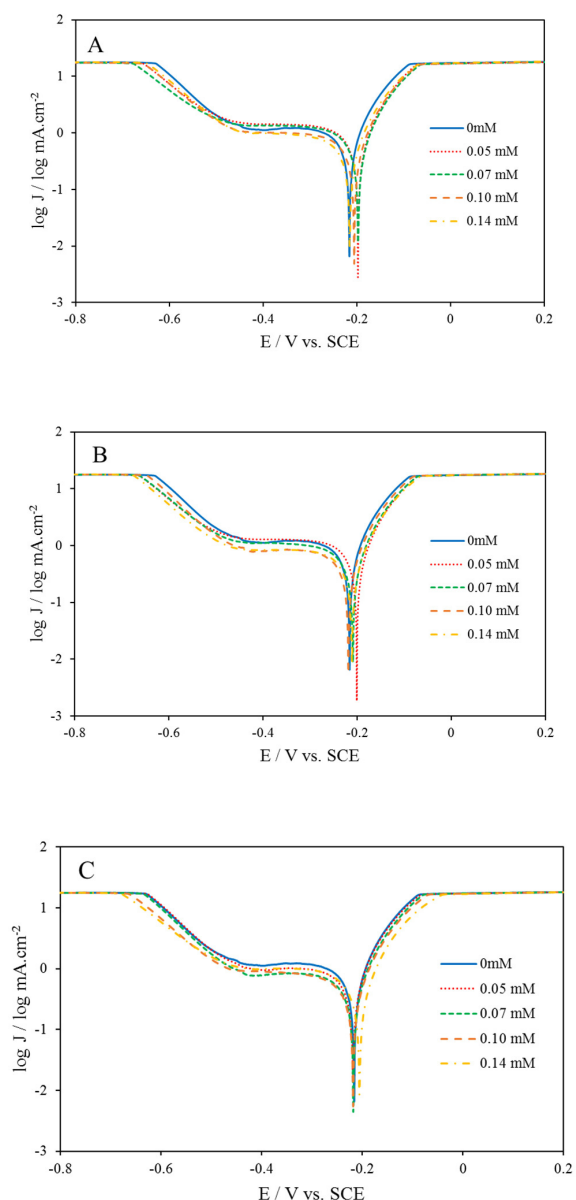


Fig. 1. Polarization curves for copper sheet in 1M HCl solution in the absence and the presence of different concentrations of the drugs (mM) at 25°C: (A) penicillin, (B) methicillin and (C) nafcillin.

The current density of corrosion lessened as the concentration of the inhibitor increased. Addition of inhibitors to HCl solution affected both the anodic and cathodic branches of the Tafel curves. Consequently, these compounds behaved as mixed inhibitors. The potential of corrosion was shifted to the negative direction more obviously. This displays that the inhibitors

effect on the cathodic half-reaction is more noticeable than on the anodic half-reaction [34]. It is clear that the inhibition efficiency of nafcillin is better than methicillin and penicillin. It is in a good agreement with the results from other studied methods.

3. 2. Weight Loss Measurement

Table 2 summarizes the results of four test runs using weight loss technique of Cu sheets corrosion in known inhibitors (0.51 mM) and acid (1 M) concentrations at 296 K for 3 h.

<Table 2>

In an overview, the inhibitors presence decreased the weight loss in acidic solutions. This is because, during the anodic process of corrosion, metal ions pass from the metal surface into the solution, and cathodic corrosion results in the discharging of hydrogen ions to produce hydrogen gas or reduction of oxygen[35].

Based on Table 2, the values of inhibition efficiency and surface coverage are found to follow the order: Blank <penicillin <methicillin <nafcillin. The maximum inhibition efficiency of 98.28% is exhibited by nafcillin, and the

Table 2. Weight loss, corrosion rate, inhibition efficiency and surface coverage for the test solutions lacking and containing an inhibitor for the corrosion of Cu sheets at 296 K for 3 h.

Inhibitor	W (g)	$A \times 10^{-3}$ ($g.cm^{-2}.h^{-1}$)	IE (%)	θ
Blank	0.0058	0.48	-	-
Penicillin G	0.0033	0.28	43.10	0.43
Nafcillin	0.0001	0.01	98.28	0.98
Methicillin	0.0027	0.23	53.45	0.53

Table 3. Weight loss and corrosion rate for the test solution contains penicillin as inhibitor for the corrosion of Cu sheet at 296 K for the two different times.

Time (h)	W (g)	$A \times 10^{-3}$ ($g.cm^{-2}.h^{-1}$)
3	0.0027	0.23
5	0.0043	0.22

minimum inhibition efficiency of 43.10% is showed by penicillin.

Table 3 displays the results of weight loss technique of Cu sheets corrosion in the known penicillin as inhibitor (0.51 mM) and acid (1 M) concentrations as a time function. By comparing the results, it is clear that the corrosion rate decreased as time progressed. It is for this reason that the accumulated corrosion products on the metal surface reduce the amount of access to the metal surface through time for corrosive agents.

3. 3. Adsorption Isotherm

The adsorption isotherm study explains the nature of the adsorption process for the inhibitor molecule on metal surfaces, providing insight into the mechanism of corrosion inhibition. The Langmuir adsorption isotherm Temkin, and Frumkin isotherms are most usually used and applied to the adsorbed species [36, 37]. In order to obtain the isotherm, the degree of surface coverage of the metal surface by adsorbed inhibitors at different concentrations of inhibitors calculated from Tafel measurements using equation (3): The plots are made to fit the values to the various isotherms mentioned above and the best fit obtained for the inhibitors is the Temkin adsorption isotherm (see Fig. 2). The Temkin[34] isotherm is given by the equation (11)

$$\ln C = -\ln K + a\theta \quad (11)$$

where θ , C , and K_{ads} are the surface coverage, inhibitor concentration, the adsorption, the interaction parameter of the absorbed inhibitors and equilibrium constant respectively [38]. The adsorptive equilibrium constant can be obtained from the intercept of the straight line in plots and the free energy of adsorption process ΔG_{ads} can be calculated from the equation (12) [39].

$$\Delta G_{ads} = -RT \ln (55.5 K_{ads}) \quad (12)$$

where the universal gas constant is R ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the thermodynamic temperature and the molar concentration of water in the solution is 55.5.

The negative values of ΔG_{ads} demonstrate that

the adsorption of inhibitors on the copper surface is a spontaneous process. The value of ΔG_{ads} around 40 kJ mol^{-1} or more negative is in agreement with the chemisorption and the ΔG_{ads} values higher or lower than 20 kJ mol^{-1} is compatible with physisorption. Physisorption involves the electrostatic interactions between the charged molecules and the charged metal while chemisorption involves electron sharing or transfer from the inhibitor molecule to the metal surface to form a coordinate type of bond [40-42].

In this work, the ΔG_{ads} methicillin, nafcillin, penicillin G are -18.71 , -18.73 and $-17.94 \text{ kJ mol}^{-1}$, respectively. These values of ΔG_{ads} show the possible electrostatic interactions of the inhibitor molecules and copper surface (physisorption).

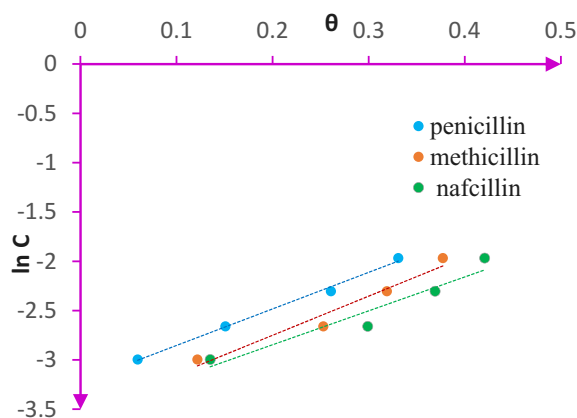


Fig. 2. Adsorption isotherms for copper in 1.0 M HCl solution at the presence of different concentrations of inhibitors from Tafel data.

3. 4. SEM Observations

The surface morphologies of the copper specimens in the presence and absence of the inhibitors are displayed in Fig. 3. The morphology of the copper specimen in the uninhibited solutions is damaged due to the corrosive attack of the acid solutions whereas in the surface with the presence of the inhibitors, the corrosion damage is visibly reduced compared to the condition of absence of the inhibitors, and

there is evidence of adsorption presence on the metal surface.

The morphology of the copper specimen in the presence of nafcillin (Fig. 3-d) is smoother than in the presence of methicillin (Fig. 3-c) and penicillin G (Fig. 3-b), indicating that nafcillin is a better inhibitor than methicillin and penicillin G.

3. 5. Spectrophotometric Measurements

UV- visible absorption spectra is a suitable method for the identification of the formation of metal complex and can be used to confirm the possibility of the formation of a protective film on the metal surface.

Abboud et al. have reported that changes in the position of the absorbance maximum and changes in the value of absorbance indicate the formation of a complex between two species in the solution [43]. The absorption spectra of methicillin and Penicillin before immersion have absorption maximums at 198nm, 288 nm, which can be attributed to π - π^* and n- π^* transitions. After copper immersion, two peaks underwent a blue shift, which may indicate formation of coordinate bonds between Cu and inhibitors. Furthermore, increase in absorbance is noticed in Cu-methicillin. The increase of absorbance suggests that there is a possibility of formation of Cu-inhibitor complex. The shape of the spectra after the immersion of Cu is not a change showing the possibility of weak interactions between penicillin and methicillin with copper (Physisorption). The results reveal that the absorbance peaks in the visible region for nafcillin decreased or disappeared after adsorption of the inhibitors on copper surface. This result gives a strong support to the possibility of the chemisorbed layer formation on Cu surface (between nafcillin and Copper).

3. 6. Computational Calculations

3. 6. 1. Quantum Chemical Calculations

The partial charges on the individual atoms in a molecule indicate the reactive centers for a particular inhibitor. The atoms with the highest

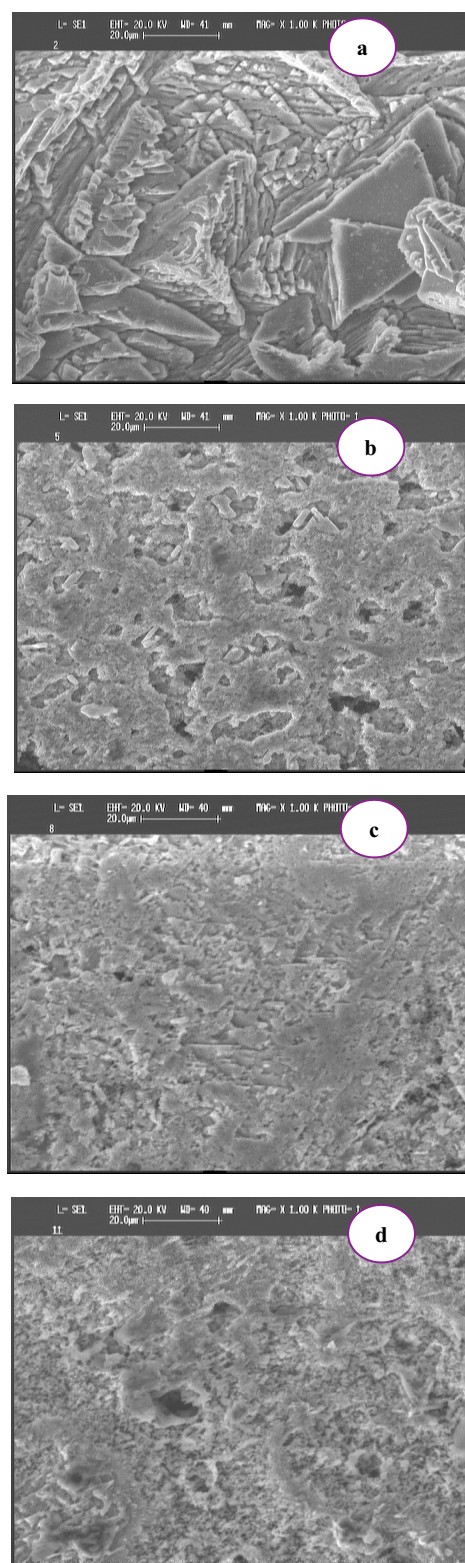


Fig. 3. SEM image of copper in 1M HCl solution after 3 h of immersion at 298 K: (a) After immersion without inhibitor; (b) In the presence of inhibitor penicillin G; (c) In the presence of inhibitor methicillin, (d) In the presence of inhibitor nafcillin.

negative charge are considered to have the highest tendency to donate electrons to the metal surface. Thus, the inhibitor is likely to interact with the metal surface through such atoms.

The binding capability of the metal on the inhibitor depends strongly on the electronic charge of the active site [44]. Each inhibitor molecule is allowed to interact with the Cu metal at the atom that has the highest negative charge.

For this purpose, Net atomic charges have been obtained using the natural population analysis (NPA). For three inhibitors, the most probable reactive site for the interaction with the metal surface are atoms that contain pairs of lone electrons because these atoms have a larger negative charge, which suggests that those active centers with excess charges could act as a

nucleophilic group.

Another parameter that is considered is the total negative charge (TNC). It is obtained by summing up all the negative charges within a molecule [13, 45]. The total negative charge for nafcillin is (-8.41) that is more than methicillin (-7.54) and penicillin G (-6.95) (Table 4). The calculations exhibited that the inhibitor with the highest inhibition efficiency has the highest TNC value which agrees well with the experimental observations.

As can be seen from the atomic charges in Table 4, the total number of charge centers (negative and positive) is calculated for the three inhibitors. The negative charge centers (NCC) could donate electrons to the Cu atoms for the generation of coordinate bonds while the positive

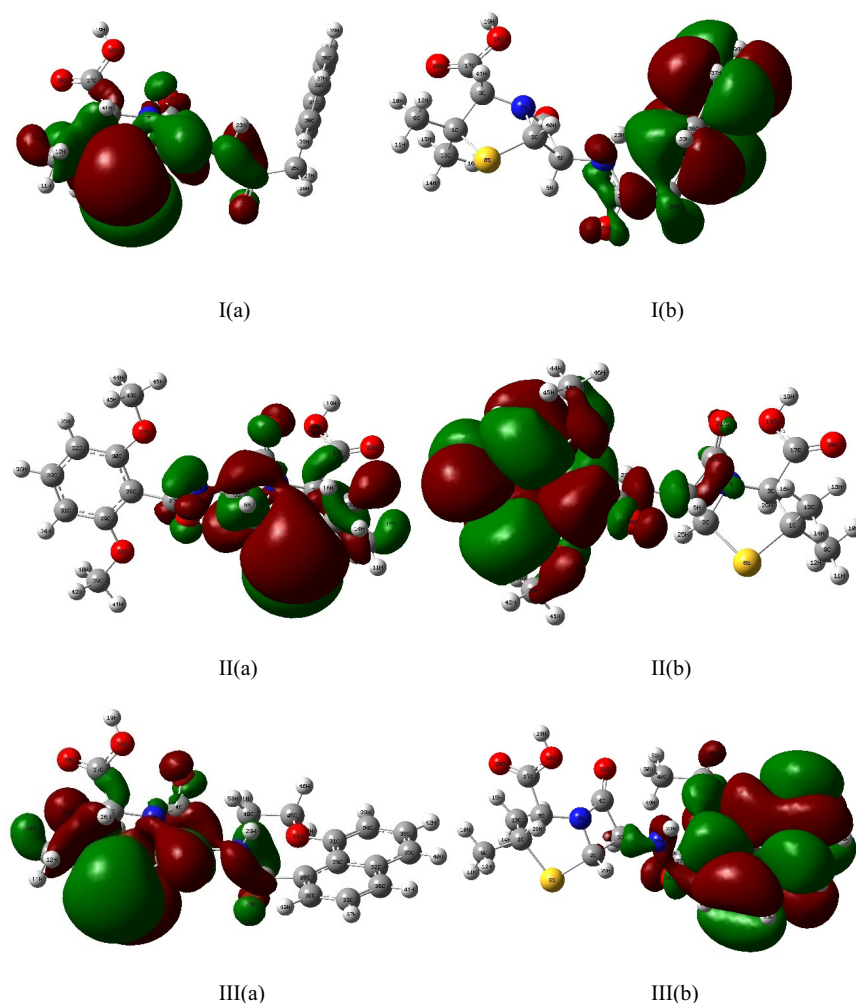


Fig. 4. The frontier molecule orbital density distribution of the investigated amines: (a) HOMO, (b) LUMO

charge centers (PCC) can accept electrons from 3d orbitals of the Cu atom to form feedback bonds, thus further strengthening the interaction of inhibitor and Cu surface. The high inhibition efficiency of nafcillin can emerge from its high number of negative charged centers of 24 and number of positive charged centers 27 (Table 4). This is confirmed as the more active sites the molecule has, the higher TNC and the higher inhibition efficiency.

The frontier orbitals electron density distributions are of the great significance in providing a full explanation of the adsorption preference of the inhibitors. The analysis of the HOMO indicates the regions of the molecule that have a tendency to donate electrons to electrophilic species whereas the analysis of the LUMO predicts the regions of the molecule with a high tendency to accept electrons from nucleophilic species. The calculated HOMO electron density distributions of the chosen three inhibitors are illustrated in Figs. 4. In three inhibitors, the HOMO is distributed strongly on five-membered thiazolidine ring and the four-membered β -lactam ring and partially on acyl amino atoms while the LUMO is especially localized on the acyl amino side-chain group.

Fukui function provides information about which atoms in a molecule have a higher tendency to either donate or accept an electron or pair of electrons. For studied inhibitors the soft-soft interactions are preferred in the site of the maximum Fukui function.

Generally, the molecular sites with large values of the $F^+(r)$ are the sites where the molecule will receive charge, when attacked by a nucleophilic reagent. On the contrary the molecular sites with large values of $F^-(r)$ are the preferred sites which the molecule will donate charge then the molecule loss electrons. For the inhibitor I, C1, C24 and C4 atoms are the most susceptible sites for accepting electrons from the metallic surface as those atoms possess the highest value of $F^+(r)$. On the other hand, the electrophilic attack would occur at S8, O25, N22, O21, C13, O18, C9, O15, O25, O20 and N7 atoms in the inhibitor I.

It is clear that for the inhibitor II the largest value of $F^-(r)$ is on the C31 and O38 and the

largest value of $F^+(r)$ is on the C17 and C4 atoms.

For inhibitor III the preferred site for nucleophilic attack is O44, O24 and C35 atoms and for the electrophilic attack is C27, C17 and C29 atoms

3. 6. 2. Molecular Dynamics Simulation

Many corrosion inhibition studies nowadays contain the use of molecular dynamics simulation as an important tool in understanding the interaction between adsorbed-metal surfaces [31, 46-48]. It has been reported that the more negative the adsorption energies, the stronger the adsorbed-metal interaction [49].

In this study, three selected inhibitors have been placed on the Cu (1 1 0) surface to find out their suitable configuration. If the system has reached an equilibrium state the fluctuations of temperature and energy should be limited to 5–10%. The Figs. 5 and 6 show temperature and energy fluctuation curve with respect to the simulation time, the temperature fluctuates in a range of (298 ± 5) K and the fluctuation of energy is less than 0.5%, indicating that the system has reached an equilibrium state [50]. The system equilibrium state and the best adsorption configuration are investigated for the inhibitor molecules on copper surface. The calculated interaction energy obtained from molecular dynamics simulation are presented in Table 4.

It is evident that values of E_{int} are negative for three inhibitors implying that the adsorption on copper surface is spontaneous. Also, from a

Table 4. The interaction energy obtained from MD simulation for adsorption of inhibitors on Cu (1 1 0) surface. the total negative charge (TNC), the total number of the negative charge centers (NCC) and the positive charge centers (PCC) of the studied inhibitors in aqueous phase calculated at B3LYP/6311++G** level

System	$E_{interaction}$ (kcal/mol)	TNC(ev)	NCC	PCC
I	-1010.6206	-6.95	19	22
II	-1083.6921	-7.54	21	25
III	-1226.7984	-8.14	24	27

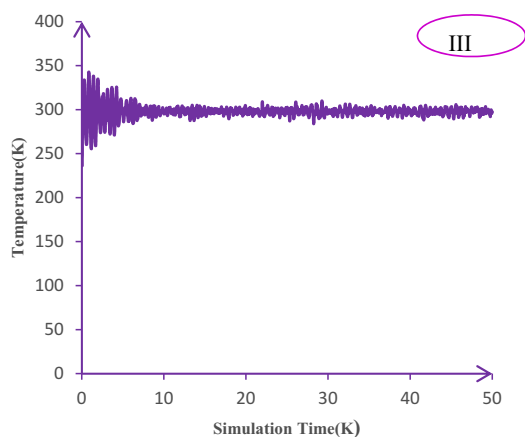
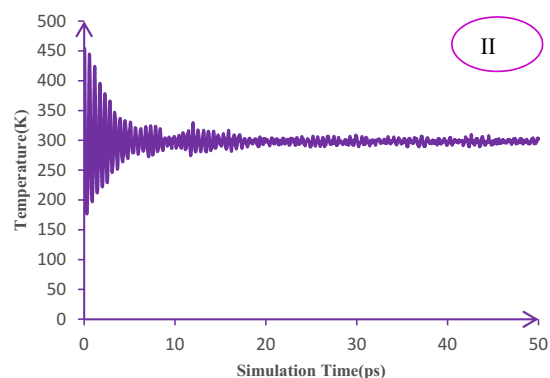
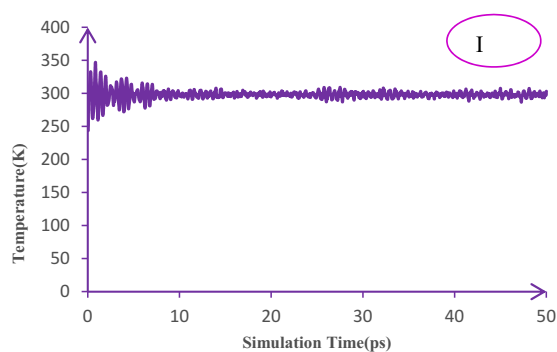


Fig. 5. Temperature equilibrium curve obtained from molecular dynamics simulation for I, II and III inhibitors.

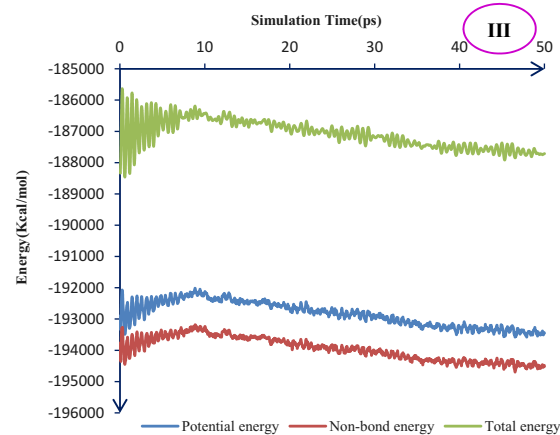
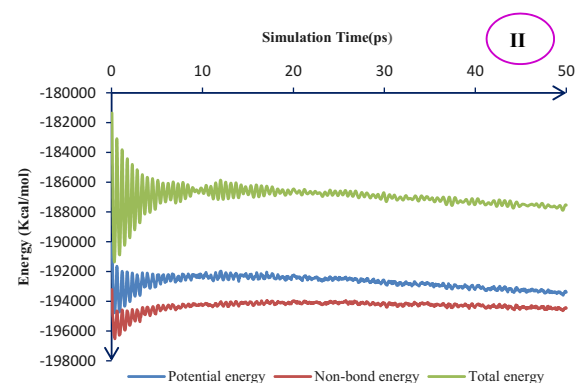
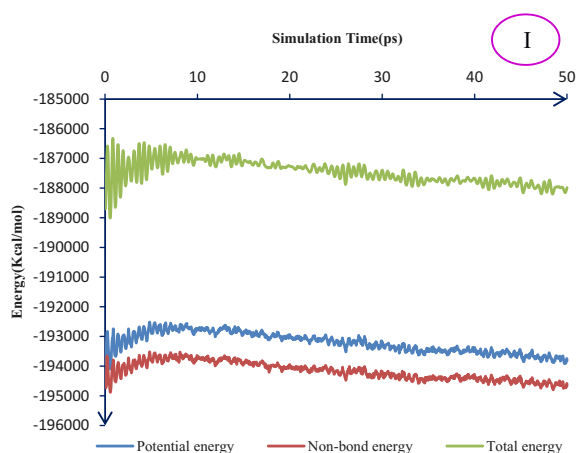


Fig. 6. Energy fluctuant curve obtained from molecular dynamics simulation for I, II and III inhibitors.

thermodynamic point of view, the more stable a system is the lower its energy state. Therefore, we expect that the more stable formed complex has the lower values of E_{int} . The interaction energy between the metal and the inhibitor is tabulated in Table 4. As can be seen, the trend follows the

order; nafcillin-Cu > methicillin-Cu > penicillin G-Cu, which confirms that nafcillin has the strongest interaction with the metal surface.

Inhibitor molecules have a parallel orientation with respect to the copper surface. The parallel adsorption configurations ensure that the copper

surface can be maximally covered by the investigated inhibitor molecules.

4. CONCLUSION

The corrosion behavior of copper was investigated in a 1 M HCl solution with and without the addition of penicillin G(I), methicillin(II), nafcillin(III) using weight loss, Tafel polarization, SEM, molecular dynamics method and quantum chemical calculations. The values of inhibition efficiency and surface coverage were found to follow the order: Blank < penicillin < methicillin < nafcillin. The maximum inhibition efficiency of 98.28% was exhibited by nafcillin, and the minimum inhibition efficiency of 43.10% was showed by penicillin. The adsorption of inhibitors on the copper surface obeyed the Temkin adsorption isotherm model. The negative value of free energy of adsorption ΔG_{ads} , indicated that the adsorption of three inhibitors is a spontaneous process. The SEM micrographs confirmed the protection of copper in a 1 M HCl solution by penicillin G, nafcillin, and methicillin. The obtained quantum chemical data showed that the most probable reactive sites for interacting the metal surface are heteroatoms. Molecular dynamics simulations were applied to find the most stable configuration and adsorption energies for penicillin G, nafcillin, methicillin molecules on the Cu (110) surface. The interaction energy followed the order: penicillin G < methicillin < nafcillin. This study displayed a good correlation between the theoretical and experimental data, which confirmed the reliability of the quantum chemical methods and molecular dynamics simulations for studying the bio-inhibition of corrosion on metal surfaces.



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