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Unused Meropenem Drug as Corrosion Inhibitor for Copper in Acidic Medium; Experimental and Theoretical Studies

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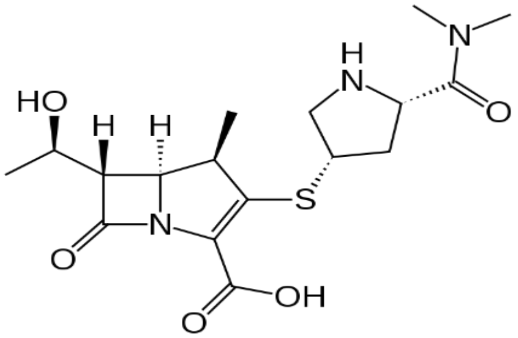
Inhibitive and adsorption properties of unused meropenem drug for the corrosion of Cu in one molar HNO_3 solution have been done by utilized (EIS), tafel polarization and (EFM) techniques as well as mass reduction methods of monitoring corrosion. The Effect of temperature was investigated at temperature range (25 - 45^0C). The obtained results indicated that the examined drug is an excellent inhibitor in 1 M HNO_3 and its efficiency equalize to 98.7% at 300 ppm. The inhibition efficiency percent (% IE) improvements with raising the drug dose while it lowering with raising the temperature of solution. The polarization data indicated that this drug play as mixed inhibitor type. The adsorption of the drug on the Cu surface follows the Temkin isotherm. Thermodynamic parameters have been calculated and discussed.

Keywords: Corrosion inhibition, Nitric acid, Copper, Unused meropenem drug

1. INTRODUCTION

The Copper metal is a good manner so it's utilized on range of applications. It is utilized in alloys, tubes, wires production, electronics, and also sheets. The utilized corrosion protective of Cu in acid medium is mainly to less the corrosion of Cu at the time of acid descaling and cleaning. The common utilized corrosive solution with HNO_3, so this medium has induced a biggest deal of study on Cu corrosion [1]. Survey of literature shows those derivatives of organic compounds such as azoles, amino acids, amines [2-17] compounds containing sulfur [18], and others given protective effect for the corrosion of copper and its alloys in various medium. It is perceive that attendance of heteroatom such as N, S, O and P in the organic molecule compound increases its action as Cu corrosion protective. This is illustrated by the attendance of vacant d orbital in Cu atom that forms coordinative bonds with atoms able to give electrons [19]. The efficiency of an inhibitor is mainly reliance on its capacity to get adsorbed on the Cu surface which contains a water molecule exchange at a corroding interface. The adsorption of organic compounds are affected by steric factor, aromaticity, electronic structure of protective molecules and electron density at donor site which attendance of functional group such as R–OH, –N=N, –CHO etc., molecular weight and area of the protective molecule as reported [20–22].The inspected drug compound display possibilities interesting for corrosion protective and particular important due to including atoms with electronegative such as S, N and O in drug compound, miscibility high in water, safe utilize, and big molecular size such these drug compounds should be perfect corrosion protective[23-30]. Many of the drugs active substances are far more cost than the organic inhibitors currently implemented. Therefore, our study was focused on the usage of expired drugs because of the patient's non-compliance that contain in their composition active substances with inhibitory properties. The utilized of unused drugs may solve two problems: lower of the costs of the expired drugs and lowering pollution environmental with the pharmaceutically active compounds. In present work the inhibitive behavior of unused meropenem for copper corrosion in one molar HNO_3 solution has been research utilized chemical and electrochemical tests. Quantum chemical measurements were utilized to illustrate the efficiency of this drug utilized as corrosion inhibitor.



5*S*,6*S*)-3-(((3*S*,5*S*)-5-(Dimethylcarbamoyl)pyrrolidin-3-yl)thio)-6-((*R*)-1-hydroxyethyl)-4-methyl-7-oxo-1-azabicyclo[3.2.0]hept-2-ene-2-carboxylic acid

Unused meropenem
Molecular formula: $C_{17}H_{25}N_3O_5S$, Molecular Weight: 383.463

2. MATERIALS AND TECHNIQES

2.1. Reagents and materials

Cu strips including (Cu: 0.001%, Al 0.004%, Ni 0.019%, Si 0.003%, Mn 0.116%, and balance Cu) were utilized for gravimetric and electrochemical research. The Cu coins were abraded utilized various grades of emery papers up to 1200 grit size, washed by double distilled water, and make dry at room temperature

2.2. Solutions

The aggressive solutions utilized were given by AR grade 70% HNO_3 (6 M) and its dose was checked utilized standardized NaOH. Appropriate dose (1 M) of acid was reading by dilution utilized double distilled water. 1000 ml stock solutions of investigated unused meropenem was obtain by dissolving an exactly weighed quantity of unused meropenem in an accurate volume of absolute ethanol, and then the required doses (50-300 ppm) were reading by dilution with double distilled water.

2.3. Experimental procedures

The mass reduction tests were done by utilized 7 parallel copper sheets of 1×1×0.2 cm were abraded with emery paper (grade 320–500–800-1200) and then washed with bi distilled water. First weight accurately then the coins were putted in a 100 ml beaker, which include 6 ml of dose of Nitric acid without and with appending of various unused meropenem dose. All the HNO_3 solutions were open system to air condition. After three hours, the coins of Cu were obtained, washed, make dry, and accurately weighed. The mean mass reduction of 7 copper parallel coins could be given. (IE %) and (θ), of unused meropenem for the corrosion of Cu were measure by the following (1)

$$IE\% = 100\times\theta = 100 \times (1-(W / W^{\circ})) \qquad (1)$$

Where, W^{o} =the data of the mean mass reduction without the drug inhibitor, W are the data of the mean mass reduction with inhibitor of drug.

Electrochemical technique were done in three electrodes cell thermostatic conventional carried by utilized a Gamry Galvanostat/ZRA/Potentiostat (model PCI 300/4),a sheet of Pt is a counter and reference electrodes were utilized by (SCE) saturated calomel electrode, the Cu electrode was in the form of a cut square from Cu electrode of size (1 x1 cm) and was accrete by one side of Cu wire utilized for connection electrical, the Cu electrode was abraded successively with different emery papers grades , rinsed with bi-distilled water and then degreased with (CH3)2CO, washed with bi-distilled water and dried finally. Electrochemical testes were done at 25°C. The diagrams for potentiostatic were occurred from -5 to 5 V at a scan with rate 0.5 mVs-1 after reached to the steady state (30 minutes), utilized for the measure of current corrosion is done by extrapolation of cathodic and anodic Tafel lines of charge transfer corrosion controlled reactions to a point which yield log $i_{corr.}$, the corresponding potential of corrosion ($E_{corr.}$) for solution blank and for each inhibitor concentration. The current corrosion density ($i_{corr.}$) was utilized to measure (θ) and (%IE) as follow (2):

$$\% \, IE = 100 \times \theta = 100 \times [1- (i^{\circ}_{corr} / i_{corr})] \qquad (2)$$

Where i_{corr} is the corrosion current in drug solutions, and i°_{corr} is the corrosion current in HNO_3.

(EIS) tests were utilized in range of frequency of 100 kHz to 10 mHz with amplitude of 5 mV. Gamry applications contain software EIS300 for EIS tests; computer was utilized for value summation. Echem Analysis 5.5 software was utilized for fitting diagrams and graphing value. The inhibition efficiency (% η) and (θ) of unused meropenem drug have been obtaining from the resistance of charge transfer data utilized the following equation (3).

$$\% \, IE_{EIS} = \theta x100 = 100 \, x[(R_{ct} - R^{*}_{ct}) / R^{*}_{ct}] \qquad (3)$$

Where R^*_{ct} are the charge transfer resistance in the HCl, and R_{ct} are the charge transfer resistances in surfactants. The interfacial double layer capacitance (C_{dl}) data were measured from the impedance data by the following equation:

$$C_{dl} = 1 / 2\pi R_{ct} f_{max}$$

Where f_{max} = maximum frequency (Hz).

(EFM) can be utilized as a fast and nondestructive experimental for rate of corrosion technique without prior information of Tafel constants. EFM performed by utilized 2 frequencies (2.0 to 5.0 Hz) [31]. The time in this work which given steady state of the specimens was found half-hour, the Intermodulation spectra include current responses form corrosion density ($i_{corr.}$) and harmonical intermodulation peaks of current. The higher peaks were utilized to measure the current, (β_a and β_c) Tafel slopes and (CF2 & CF3) causality factors. All the experiments were conducted at room temperature.

3. RESULTS AND DISCUSSION

3.1. Gravimetric techniques

The mass reduction of Cu specimen in one molar HNO_3 solution, attendance and absence of various dose of unused meropenem was measured after putted 3hrs at 25°C. Figure (1) represents this for unused meropenem. Data given from % IE are written in Table (1). The attendance of unused meropenem drug lowers the corrosion rate of Cu in one molar nitric acid. The %IE was obtained as improve with rising the temperature.

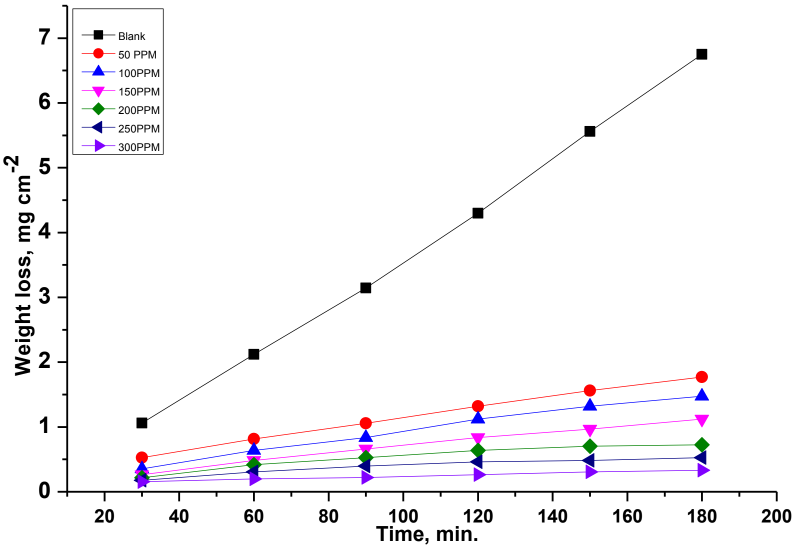


Figure 1. Time -mass reduction diagrams for the corrosion of Cu in 1 Molar Nitric acid in the presence and absence of various dose of unused meropenem at room temperature

Table 1. (C.R.) mgcm^{-2}min^{-1} and (I.E %) value given from mass reduction test for Cu in 1 molar Nitric acid solutions in absence and attendance dose of unused meropenem at 25°C

Conc., ppm	C.R., (mgcm^{-2}min^{-1})	% IE
------	0.0360	---
50	0.0050	84.7
100	0.0040	88.0
150	0.0030	90.5
200	0.0025	92.4
250	0.0020	93.5
300	0.0010	94.6

Table 2. Value of mass reduction results for Cu in 1 molar Nitric acid solution in the attendance and presence various dose of unused meropenem at 25–45°C

Conc., ppm	C.R., (mgcm^{-2}min^{-1})				
	25^0 C	30^0 C	35^0 C	40^0 C	45^0 C
1M HNO_3	0.0360	0.0560	0.1010	0.1350	0.3240
50	0.0050	0.0090	0.0180	0.0280	0.0740
100	0.0040	0.0080	0.0160	0.0260	0.0680
150	0.0030	0.0060	0.0130	0.0200	0.0580
200	0.0025	0.0050	0.0100	0.0160	0.0510
250	0.0020	0.0040	0.0090	0.0130	0.0350
300	0.0010	0.0030	0.0070	0.0110	0.0290

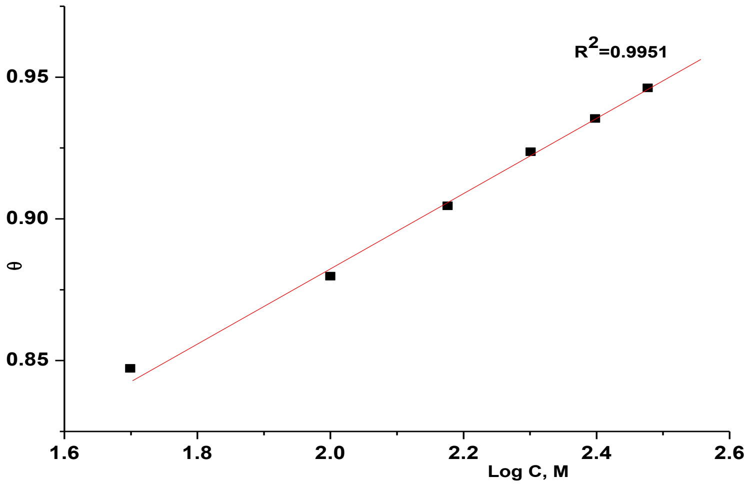


Figure 2. Temkin isotherm curve for Cu in one molar Nitric acid with inconsistent dose of unused meropenem at 25°C

The interaction degree and mode between unused meropenem drug inhibitor and Cu surface have been broadly obtained with the isotherms applied. The unused meropenem molecule adsorbed due to the energy interaction between it and a metallic copper surface is biggest than that between water molecules and surface of copper [32]. The data obtain for surface cover θ were measured at various dose of unused meropenem in one molar HNO_3 solution. The data of θ were drawing to fit the suitable model of adsorption. Experiments were study to fit value of tests to inconsistent kind of isotherms contain Langmuir, Frumkin, Freundlich and Temkin isotherms. By far the data were best fitted by isotherm Temkin in Figure (2). ($\Delta G°_{ads}$) the standard free energy of adsorption is depending on (K_{ads}) equilibrium constant utilized the following equation [33]:

$K_{ads} = 1/55.5 \exp [-\Delta G°ads/RT]$ (4)

Figure (2) give the drawing of (θ) versus log C for unused meropenem. By adding to, the degree of inhibition is directly depending on the performance of layer adsorption which is a sensitive to the molecular structure. The ΔG^o_{ads} = 11.4 kJ mol^{-1}, K_{ads} = 7.5 M^{-1} and 'a' is the heterogeneity factor, its sign is positive and equal to 17.8. This positive value of 'a' indicates that there is an attraction among the adsorbed molecules on Cu surface. The lower negative values of ΔG^o_{ads} indicates that unused meropenem is strongly adsorbed physically on Cu surface at ranges of temperature research but the adsorption lower with the higher in temperature. The –ve data of ΔG^o_{ads} ensure the spontaneity of the adsorption. The biggest data of K_{ads} lead to the strong adsorption of the unused meropenem on Cu surface.

Mass reduction method was achieved at various temperatures (25°C–45°C) in the attendance of various dose of unused meropenem. Given the corrosion rate increases with the temperature raise for unused meropenem Table (2). The rate of Cu corrosion without unused meropenem rises from 25 to 45°C whereas; with unused meropenem the corrosion rate limits decrease. (I.E%) was given improvement with temperature. The apparent activation energy ($E*_a$) for liquefaction of copper in one molar nitric acid was measured from the slope of draw by utilized Arrhenius (5):

$C.R = A \exp^{(-Ea*/ RT)}$ (5)

Where T = the absolute temperature, A = the Arrhenius constant, k = the rate of corrosion and R = the constant universal gas. By drawing 1/T versus log k the data of (E^*_a) has been estimated (E^*_a = (slope) 2.303 x R) Figure (3). (E^*_a) Activation energy for the Cu reaction in 1molar Nitric acid rises with attendance of unused meropenem Table (3), this improving in E^*_a lead to the formation of energy barrier, the degree of the rate rise with higher inhibited solution than the free 1molar Nitric acid solution, (I.E%) of unused meropenem improve directly with raising temperature, this result agree with the fact which state the adsorption of unused meropenem drug components on the Cu surface may be nature chemical, as the temperature raised the number of adsorbed molecules also improve given higher in the (I.E%) and the obtained results suggest that unused meropenem inhibits the reaction of corrosion by rising its E^*_a. This could be illustrated by adsorption on the Cu surface given a barrier for mass and charge transfer. Moreover, the relatively decrease of data for activation energy with unused meropenem lead to a chemical adsorption process. The data of (ΔH^*) and (ΔS^*) can be measured by equation (6), as follow:

$k = (R T/Nh) \exp (\Delta H*/RT) \exp (\Delta S*/R)$ (6)

where , h = constant Planck's, ΔH* = the enthalpy of activation, k = rate of corrosion, N = Avogadro number and ΔS* = the entropy of activation. A drawing of log (k/T) against 1/T Figure (4) give a straight line, with an intercept equal [log (R/Nh)+ ΔS^*/2.303R] and a slope equal (ΔH^*/2.303R), from which the data of ΔH^* and ΔS^* can be measured Table (3) the –ve sign of ΔS^* for the inhibitor lead to activated complex in the rate determining step(RDS) observed an association rather than a dissociation step, , the -ve sign of ΔH^* lead to the adsorption of unused meropenem is an exothermic process[35].

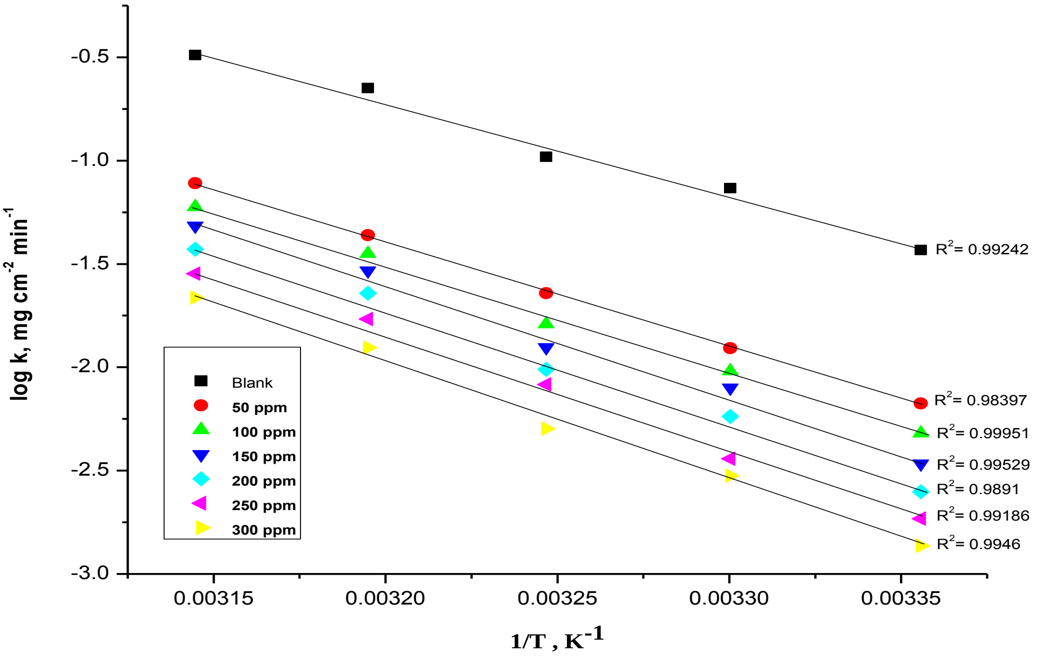


Figure 3. 1/T vs. log k (corrosion rate) plots for Cu in 1 molar Nitric acid in the presence and absence of inconsistent dose of unused meropenem

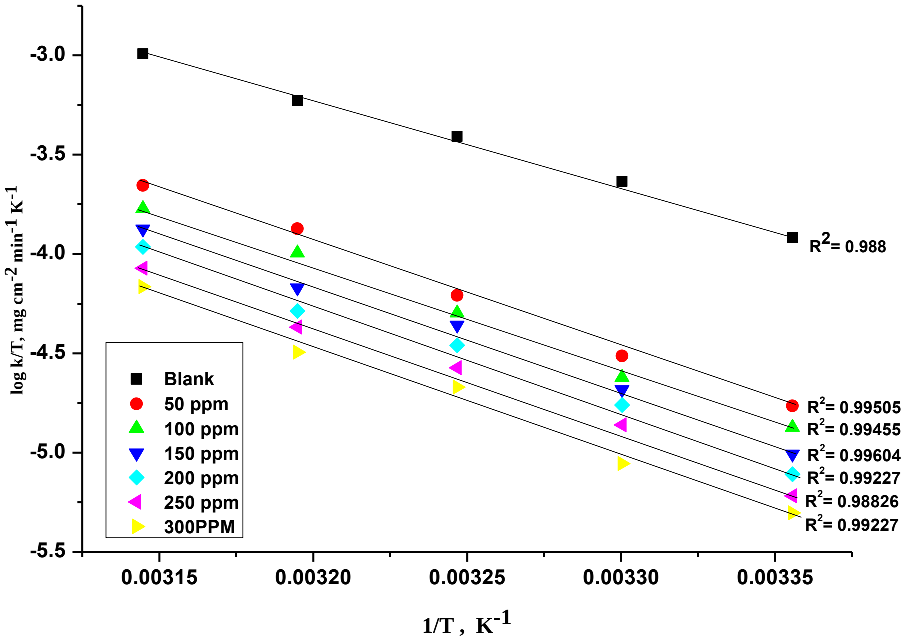


Figure 4. 1/T vs.log k /T plots for Cu in one Molar Nitric acid in the presence and attendance of inconsistent dose of unused meropenem

Table 3. Activation parameters for dissolution of Cu with and without inconsistent dose of unused meropenem in one molar Nitric acid in the range of 25-45^{o}C

Conc., ppm	E_a^* kJ mol^{-1}	ΔH^*- kJ mol^{-1}	ΔS^* Jmol^{-1}K^{-1}
------	83.1	36.1	147.2
50	107.4	46.6	115.6
100	108.3	47.0	111.6
150	109.7	47.7	105.2
200	110.5	48.0	93.8
250	111.2	48.3	86.9
300	115.5	50.2	63.9

3.2. Tafel polarization tests

Depending on theory of corrosion [36], the rightward change of the cathodic diagrams lead to that corrosion is mostly speed by cathode reactions. Hence, HNO_3 is a biggest Cu oxidizer capable of accelerate attacking on Cu.

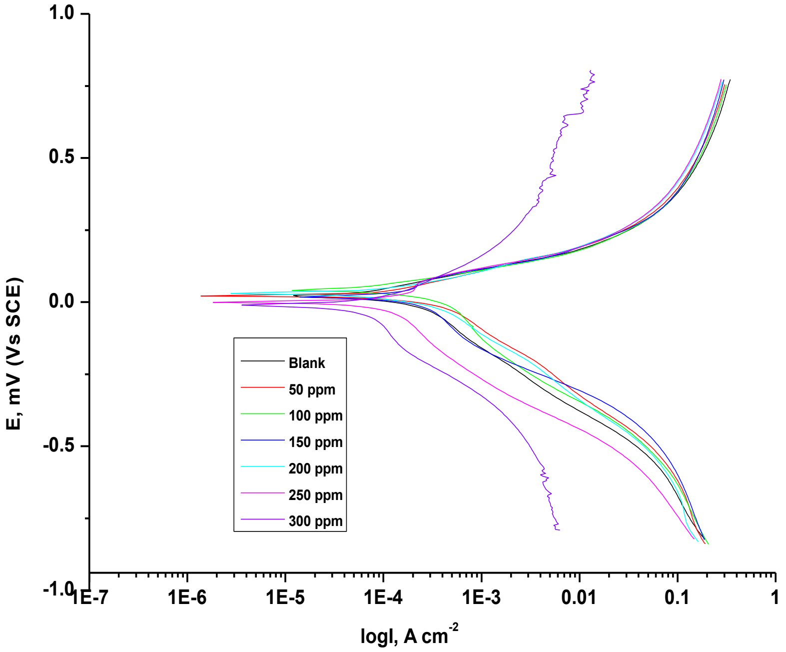


Figure 5. Diagram of tafel for the copper corrosion in one molar Nitric acid with and without different dose of unused meropenem at room temperature.

The tafel polarization diagrams illustrated no steep slope in the anodic average. Cu may directly dissolve in one molar HNO_3 solutions [37-38] that the Cu is damaged to Cu^{2+} in nitric acid solutions. The electrochemical reactions for Cu in nitric acid solution can be drawn as follows: Anodic reaction:

$$Cu \rightarrow Cu^{2+} + 2e- \qquad (7)$$

The corrosion of Cu in one molar HNO_3 contains reduction of the nitrate ion (Eqs. 8 and 9). In aerated nitric acid solutions, liquefaction oxygen may also be reduce Cu surface [39]

$$3H^+ + NO_3^- + 2e- \rightarrow H_2O + HNO_2 \quad (8)$$

$$4H^+ + NO_3^- + 3e- \rightarrow 2H_2O + NO \quad (9)$$

$$4H^+ + O_2^- + 4e- \rightarrow 2H_2O \quad (10)$$

The tafel polarization (anodic and cathodic) plots for Cu corrosion attendance and lack various dose of the investigated unused meropenem at 25ºC was research. It shows that with improvement dose of drug, I_{corr} lower considerably as compared to one molar HNO_3 and the IE is raised as the unused meropenem dose is rise. It is noted that, rising in unused meropenem lower both the cathodic and anodic current densities. Figure (5) Given tafel polarization manner of Cu in nitric acid attendance and lack various dose of the unused meropenem. No definite change in corrosion potential, E_{corr}, was obtained in attendance of the unused meropenem drug as compared to uninhibited solution thereby lead to the investigated unused meropenem drug may be define as mixed-kind inhibitors.

Table 4. Effect of dose of unused meropenem on the parameters of electrochemical measured utilized by potentiodynamic polarization method for the corrosion of Cu in 1 molar Nitric acid at room temperature

Conc., Ppm	$-E_{corr}$ mV vs SCE	I_{corr} μA cm^{-2}	β_C mV dec^{-1}	β_a mV dec^{-1}	C.R mpy	θ	%IE
Blank	42.5	208.0	234.2	100.1	200.5	-----	-----
50	14.2	116.0	319	130	59.46	0.442	44.2
100	18.0	73.3	316	129	37.54	0.648	64.8
150	18.6	71.70	375	189	36.75	0.655	65.5
200	22.4	58.3	293	115	29.87	0.720	72.0
050	24.2	46.2	259	103	23.67	0.778	77.8
300	34.6	13.1	161	92	6.69	0.937	93.7

3.3. EIS tests

EIS given a new technique for characterizes the coverage film on the metal electrode which is lead to charge resistance transfer (R_{ct}). The interface capacitance can also be utilized to calculate the film quality [40-46]. Form observed result given that the organic substance wrap on the surface of metal rely not only on the metal nature and the unused meropenem structure, but also on the conditions of experimental such as concentration of adsorbent and immersion time [47]. Figure (6) give the Nyquist (a) and Bode (b) curves obtain from open-circuit potential both without and with increasing dose of investigated meropenem at 25°C. Figures (6a) give a similar type of Nyquist draw for Cu with unlike dose of the unused meropenem. The attendance of half semi-circle single lead to the charge transfer single process due to liquefaction of Cu metal surface which is unimpressed with unused meropenem inhibitors. All the EIS were calculated at the consentient open-circuit potentials. The

Nyquist unused meropenem diagrams from different half semicircles are draw as expected from the EIS theory which due to disappear of frequency. Examination of the resulted given that each impedance plots include of a higher capacitive loop with one time capacitive constant in the Bode – phase curves Figure (6b). The diameter of the loop improves with rise dose and lead to the inhibition percent of the process corrosion.

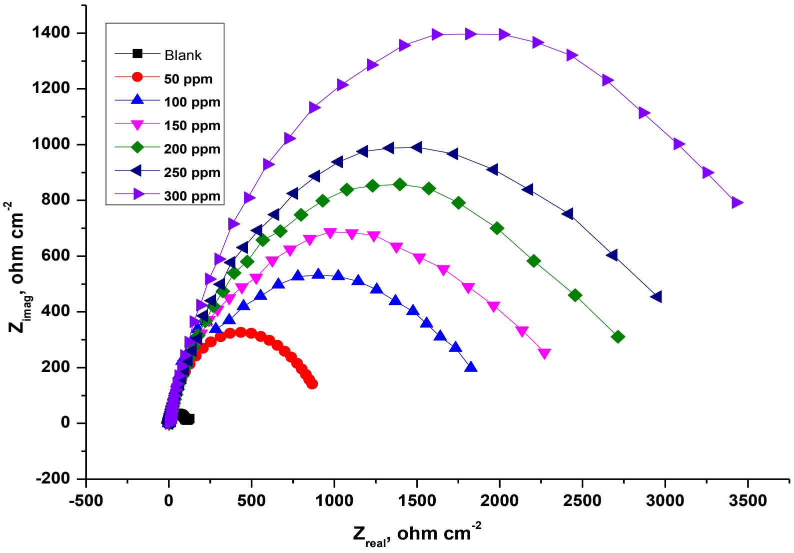


Figure 6a. Nyquist plots showing effect of increments concentration of meropenem on corrosion of Cu in 1 molar HNO_3

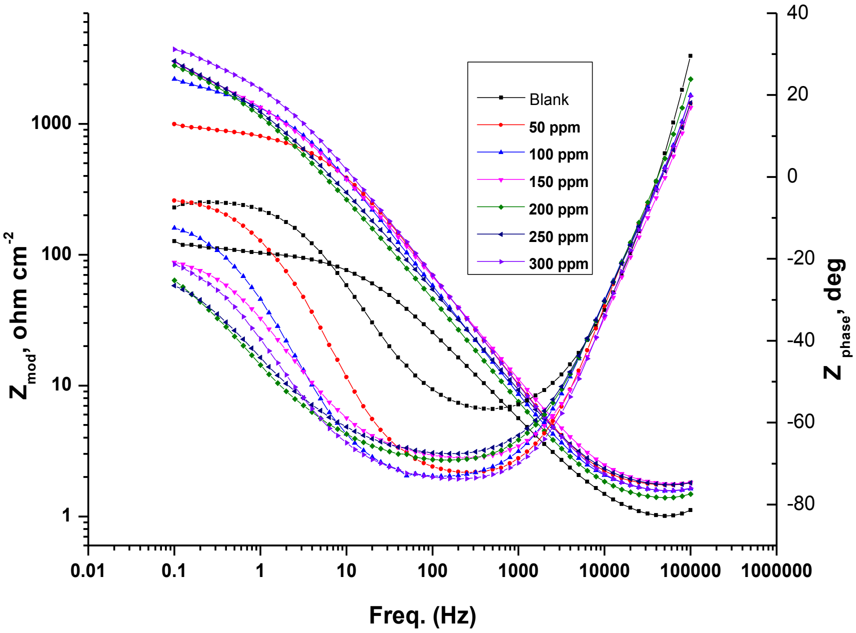


Figure 6b. Bode plot for corrosion of copper in 1 molar Nitric acid attendance and lack dose of meropenem at 25°C

The equivalent electrical circuit model give in Figure (7) was utilized to measure the obtained impedance value. The model contains of the resistance charge-transfer of the corrosion interfacial reaction (R_p) or (R_{ct}),the resistance solution (R_s)and the double layer capacitance (C_{dl})[48].

EIS data in Table (5) give that the R_{ct} data rise and the C_{dl} data lower with raise the inhibitor doses. This is due to the gradual water molecules replacement by the adsorption of the molecules inhibitor on the surface of metal, lowering the extent of liquefaction reaction. The rise R_{ct} data are generally associated with little corroding system [49-50]. The lower in the C_{dl} can result from the low of the local dielectric constant and/or from the rise of electrical double layer thickness [51-52]. (IE %) is measured from the charge–transfer resistance value as shown in equation 3 [53]. The %IE given from EIS resulted are close to those obtain from polarization technique.

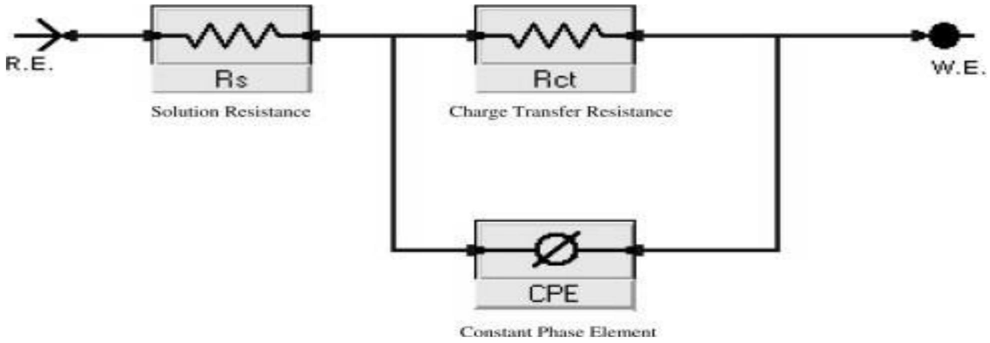


Figure 7. Equivalent circuit model utilized to fit the spectra of EIS.

Table 5. Resulted from EIS measurements for corrosion of copper in 1molar Nitric acid solutions at unlike dose of unused meropenem at 25°C

Conc., Ppm	R_s Ωcm^2	$Y_{x10}{}^{-6}$	$n_{x10}{}^{-3}$	R_p Ω cm^2	C_{dl} μFcm^{-2}	θ	IE%
Blank	0.927	773.1	756.8	109.4	348.0	-----	-----
50	1.649	147.68	862.0	885.1	600.6	0.876	87.6
100	1.54	110.44	847.0	1900	83.60	0.942	94.2
150	1.588	96.70	791.0	2409	65.80	0.955	95.5
200	1.256	83.30	788.9	2842	56.60	0.962	96.2
250	1.559	75.20	772.0	3009	48.80	0.964	96.4
300	1.451	69.27	839.0	3313	43.50	0.967	96.7

3.4. EFM test

EFM is a nondestructive and linear corrosion method that can directly calculated the current point of corrosion with only a small polarizing signal and without earlier Tafel slopes knowledge, these EFM technique advantages given it as ideal technique for corrosion monitoring online. Intermodulation spectra given from EFM calculation are obtain in Figure (8) are copper examples on solution of acid devoid of and Figure (9) containing 300 ppm dose of unused meropenem at 25° C. Each spectrum is a current reply as a frequency function. The 2 biggest peaks are the reply to the 2 Hz and 5Hz excitation frequencies. These peaks are utilized by the EFM 140 software package to measure the current corrosion. The measured corrosion kinetic parameters at unlike dose of the unused meropenem in one malar nitric acid at 25° C ($i_{corr.}$, β_a, β_c, CF-2, CF-3 and % IE) are obtained in Table 5 which contain corrosion current densities lower and the inhibition efficiencies rise by increment the dose of the unused meropenem, very close causality factors in Table (6) to theoretical value [54] the validity of data depend on the CF-2 and CF-3 are 2.0 and 3.0, respectively, leading to the calculated point are of good.

The inhibition efficiencies IE_{EFM} % improvements by raise the concentration of unused meropenem drug and measured from equation (13) as follow:

$$IE\,\%_{EFM}=(1-i_{corr}/i_{corr}^{\circ})\times 100 \qquad (13)$$

Where , i^{o}_{corr} and i_{corr} = corrosion current densities with and without unused meropenem, respectively. The obtained data showed are in good agreement of kinetic parameters corrosion obtained from the EIS and Tafel extrapolation methods.

Table 6. Parameters given by EFM method for Cu in attendance and lack various dose of the unused meropenem at 25oC

Con., ppm	I_{corr} μA cm^2	β_a mVdec^{-1}	β_c mVdec^{-1}	CF-2	CF-3	C.R. mpy	Ɵ	IE
Blank	265	90.510	323	1.92	2.53	135.70	----	----
50	24.08	71.850	188.8	1.89	2.27	23.21	0.909	90.9
100	8.13	73.640	129.9	1.69	3.16	7.84	0.969	96.9
150	6.743	55.140	110.5	1.79	3.69	6.50	0.975	97.5
200	6.476	52.210	87.09	1.69	3.65	6.24	0.976	97.6
250	5.554	44.990	59.65	1.79	4.07	5.35	0.979	97.9
300	3.508	45.070	57.65	1.34	3.91	3.38	0.987	98.7

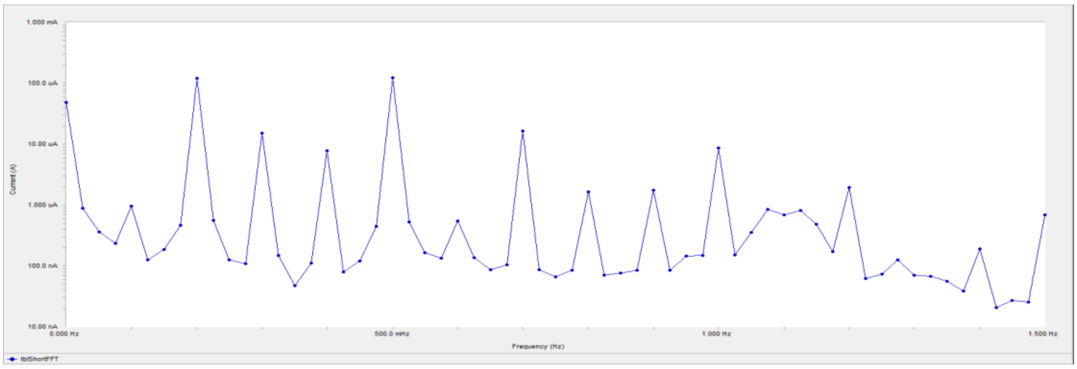


Figure 8. EFM plots for the Cu corrosion in one molar Nitric acid at 25^{0}C

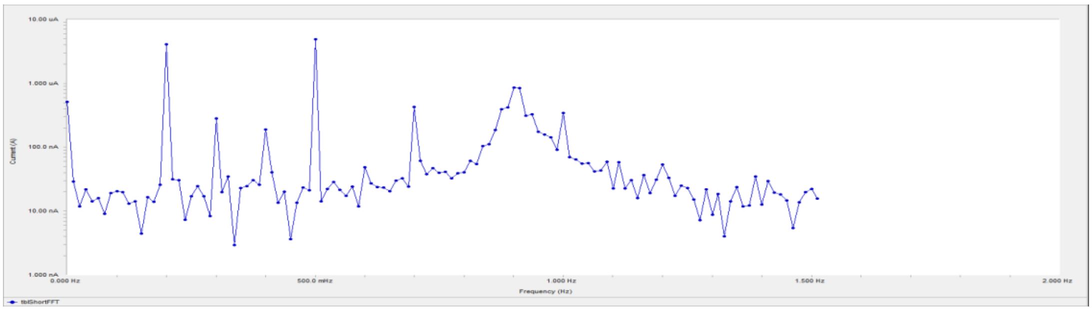
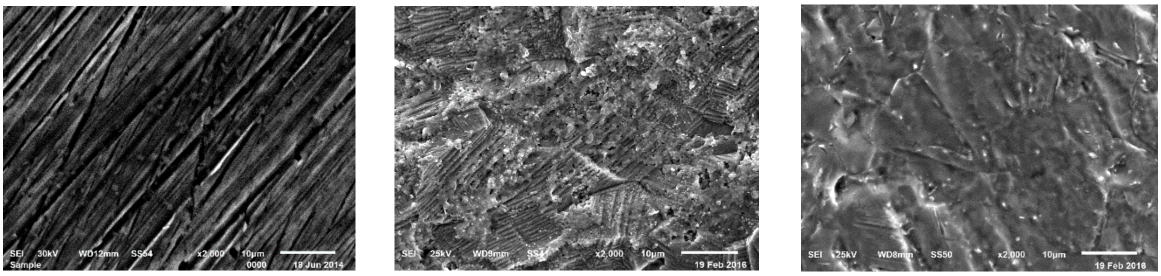


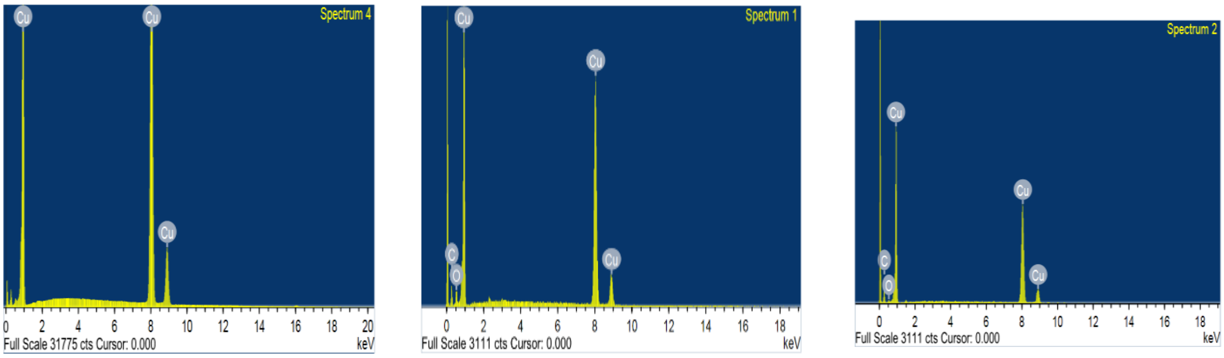
Figure 9. EFM spectra for Cu dissolution in one molar Nitric acid in the presence of 300 ppm unused meropenem at 25^0C

3.5. Surface analysis



10a 10 b 10 c

Figure 10. SEM figure of copper surface (a) before of putting in 1 molar Nitric acid, (b) after 8 hr of immersion in 1 molar Nitric acid, (C) after 8 hr of putting in 1 molar Nitric acid +300 ppm of meropenem at 25^0C



11 a 11b 11c

Figure 11. EDX spectra of Cu surface (a) before of putting in 1 molar Nitric acid, (b) after 8 hrs of putting in: 1 molar Nitric acid, (c) in 1 M HNO_3+ 300 ppm meropenem at 25° C.

SEM and EDX tests were study to determine if the meropenem drug is in fact adsorbed on Cu surface or just peeled off the surface. SEM image lead to of the changes that accompany both corrosion and inhibition of the Cu surface (Fig. 10 a–c). Figure 10a gives the Cu free. Figure 10b gives the damage due to the surface immersion one molar nitric acid. (Fig.10c) gives SEM image of the Cu surface after immersion with one molar HNO_3 with 300 ppm of meropenem. From these SEM image, it is obvious that the Cu surface seems to be almost unaffected by corrosion. Due to adsorption of meropenem which was forming a thin inhibitor film of the drug on the Cu surface. The corresponding EDX profile experiment are attendance in (Table 7) and (Figure 11) for meropenem attendance and lake of 300 ppm drug.

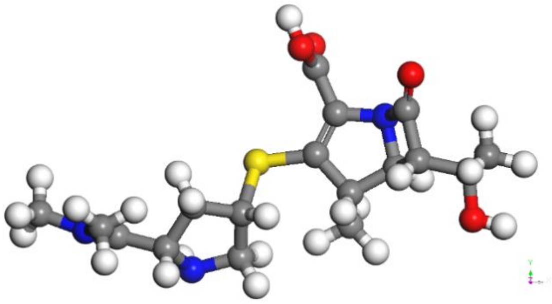
It is obvious from the EDX spectra of Cu in the attendance of meropenem, the appearance of C,O,N peaks (Figure (11)) which suggest the meropenem adsorption on the Cu surface and corroborate the thin inhibitor film formed and given in SEM micrograph.

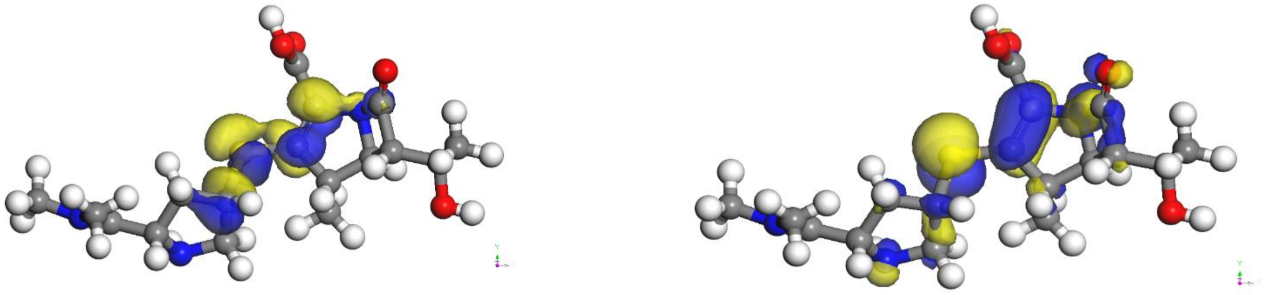
Table 7. Composition of surface (weight %) of copper after 8 hrs of putting in 1 molar Nitric acid + 300 ppm unused meropenem

Mass %	Cu	C	O
Pure	100	---	---
Blank	73.39	21.15	5.46
meropenem	65.52	32.24	2.23

3.6. Quantum methods

Mulliken charges





LOMO HOMO

Figure 12. Molecular orbital diagrams and Mulliken charges of meropenem.

Figure 12 give the molecular orbital diagrams and Mulliken charges of meropenem. Theoretical measurements were utilized for only the neutral forms, in order to obtain further insight into the experimental data. Results from quantum theory lead to such as (LUMO) lowest unoccupied molecular orbitals energies and (HOMO), (ΔH_f) the genesis heat and (ΔE) energy gap, are measured by semi-empirical PM3 technique has been show Table (8). It has been record that the higher, i.e less -ve E_{HOMO}, in addition, the decrease E_{LUMO}, the easier the gain of electrons from Cu surface [55, 56]. From Table (8), observed that ΔE given enhance the assumption that meropenem molecule will be absorbed strongly on Cu surface, because easy of electron transfer among molecular orbital HOMO and LUMO which occurring during its adsorption on the Cu surface and thereafter attendance the maximum of inhibition efficiency. Reportedly, excellent corrosion inhibitor is usually this pharmaceutical compound drug and which do not only offer electrons to unoccupied orbital of the Cu surface, but also gain free electrons from the Cu [57]. It can be seen that all results for quantum chemical (Theoretical measurements) parameters validate our experimental data.

Table 8. The calculated quantum chemical properties for investigated compounds

$-E_{HOMO}$	$-E_{LUMO}$	$\Delta E = E_{LUMO} - E_{HOMO}$	$\eta = \Delta E / 2$	$\sigma = 1/\eta$	$-Pi = (E_{HOMO} + E_{LUMO})/2$	$\chi = -Pi$	Dipole moment
9.446	0.93	8.516	4.258	0.235	5.188	5.188	10.837

3.7. Inhibition mechanism

It clear from the experimental results that the meropenem drug is physically adsorbed on Cu surface and act as a fundamental point in inhibition process. The inhibitive effect of the meropenem drug may be attributed to the accumulation of the inhibitor molecules on to the Cu surface, which lower the direct contact of the metal with the corrosive environment [55]. The meropenem drug may be adsorbed on the positively charged surface of Cu in the form of neutral molecules, contain movement of water molecules from the Cu surface and sharing electrons among oxygen, nitrogen atoms and the surface of Cu [56]. Furthermore, adsorption can study via adsorbed anion NO_3^- at the +ve charged copper surface. The adsorbed NO_3^- anion makes a negatively charged double layer and consequently it results in improve in the adsorption capability of the protonated meropenem drug molecules on Cu surface.

4. CONCLUSIONS

From the overall data results the following conclusions can be obtained:

Meropenem is best corrosion inhibitor and acts as mixed type for Cu corrosion in one molar

HNO_3. The results given from all analyses lead to the inhibiting action rise with the meropenem drug dose and lower with the rise in temperature. Double layer capacitances lower with respect to blank solution when the meropenem drug is added. This fact confirms the adsorption of the meropenem drug molecules on the Cu surface. The adsorption of the meropenem drug on Cu surface in one molar HNO_3 solution obeys Temkin adsorption isotherm. The -ve data of the ΔG^o_{ads} and adsorption heat are lead to that the process was exothermic and spontaneous. The data of inhibition efficiency which given from the unlike independent quantitative techniques utilized have shown the validity of the result data.

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