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An Expired Non-Toxic Diltiazem Hydrochloride as Corrosion Inhibitor for Cu in Nitric Acid Medium

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The corrosion inhibition of Cu in 1 M HNO_3 solution by expired Diltiazem Hydrochloride (HD) has been tested by Tafel polarization, electrical frequency modulation, electrical impedance spectroscopy, and mass loss method. The Diltiazem Hydrochloride gives 86.5 % protection efficiency at optimum dose at 300 ppm. DILTIAZEM HYDROCHLORIDE PP studies suggest that it is mixed kind inhibitor. EIS technique was also utilized to give the corrosion inhibition mechanism. The adsorption of the Diltiazem Hydrochloride on Cu surface was found to follow the Temkin's isotherm. Some adsorption parameters and thermodynamic activation were measured to given the corrosion protection mechanism. The relationship among the IE and some quantum calculation have been computed and argument.

Keywords: Copper, Expired Diltiazem Hydrochloride, Acidic medium, Quantum chemical calculations

1. INTRODUCTION

Copper has wide applications in electronic manufactures and connection as heat exchangers and conductors, pipelines for domestic and manufacture water utilities contains water, a conductor in electrical strong lines, giving its maximum conductivities in electrical and thermal, noble relatively properties and its mechanical workability. Therefore, corrosion of Cu and its protection in a great different medium have been important in many investigators [1- 10]. The great known techniques for protection corrosion are utilized inhibitors to mitigate the reduction of useful quality of alloys due to corrosion when they assault electrochemically or chemically by its natural environment. The construction of the inhibitor is one of the basic factors that affect the interaction among inhibitor and metal[11]. For Cu, which can give many-bonds, inhibitor molecules include sulphur and nitrogen atoms are recommended power. Among the S, N or O including organic assembled is the heterocyclic structure which are affect on inhibitors for corrosion of Cu in aqueous medium[12].Heterocyclic assembled including the group of mercapto have also been progress as inhibitors for Cu for unlike manufactures applications [13]. Azole assembled includes N atoms, which react with Cu among the electrons lone pair to give complexes (Cu-azole) [14]. These complexes are believed commonness to be polymeric in form and nature protective film adherent on the Cu alloy, which play as a barrier to attraction ions such as chloride. In new papers, various thiadiazole derivatives [15-22], have been recorded as best inhibitors for Cu and Cu alloys corrosion in unlike corrosive medium.Due to the toxicity of largely utilized corrosion protection, there are large interest in exchange harmful inhibitors with helpful non-hazardous. The use of Diltiazem Hydrochloride s offers interesting possibilities for corrosion protection because attendance of its hetero atoms in their molecules, and they are of particular important due to their safe utilize, water solubility maximum and large size of molecule. Some of the azosulpha and ant malarial Diltiazem Hydrochloride s have been research as best corrosion protection [23-25].Most of Diltiazem Hydrochloride s are costly than most investigated organic inhibitors utilized. Therefore, our research was centering on the utilized of expired Diltiazem Hydrochloride s due to patient's non-compliance that include in their assembled active substances with inhibitory characteristics. These investigated unused Diltiazem Hydrochloride s can give the limitation of environmentally active assembled and loss of the disposal expensive of unused Diltiazem Hydrochloride s. In this paper, the expired (HD) Diltiazem Hydrochloride has been selected to study anticorrosion on Cu in 1 M HNO_3solution utilized some electrochemical and chemical tests. This compound is nontoxic and inexpensive.

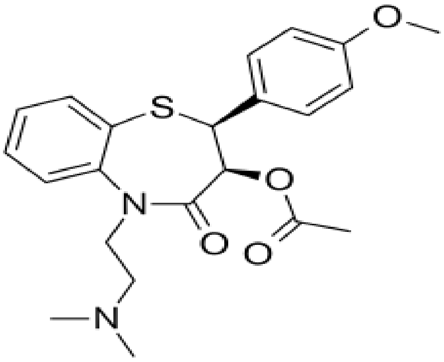
2. MATERIALS AND METHODS

2.1. Composition of Cu specimens

Cu used in this paper has the following composition in weight %:0.001 Ni, 0.019 Al, 0.004 Mn, 0.116 Si and balance Cu

2.2. Solutions

The solution aggressive utilized was made of analar grade HNO_3 and its dose was examine utilized standardized sodium hydroxide. 1 M of acid was prepared by diluting using bidistilled water. 1000 ppm stock solution of Diltiazem Hydrochloride was prepared by dissolving 1 g of the Diltiazem Hydrochloride in one Liter bidistilled water, then the need 50 – 300 ppm dose were ready by dilution. The structure, name, and formula of Diltiazem Hydrochloride used in this study were listed below:



Diltiazem Hydrochloride ([(2S,3S)-5-[2-(dimethylamino)ethyl]-2-(4-methoxyphenyl)-4-oxo-2,3-dihydro-1,5-benzothiazepin-3-yl] acetate; hydrochloride

Molecular formula: $C_{22}H_{27}ClN_2O_4S$, Molecular weight: 450.97878 g/mol

2.3. Experimental

The WL tests were occurred utilized Cu coins each of size 20 x 20 x 2 ml. The coins were polished, washed, and weighted then putted in 100 ml solution of nitric acid attendance and lack of unlike dose of Diltiazem Hydrochloride for three hours. Finally, the coins were immersed in bi-distilled water, dried, and weighed; the (%IE) and (θ) of Diltiazem Hydrochloride on the Cu corrosion were measured in equation (1):

$$\%IE = 100x\ \theta = [(W_u - W_i) / W_u] \times 100 \quad (1)$$

Where W_u and W_i are the mass reduction attendance and with Diltiazem Hydrochloride, severally. All electrochemical tests were carried out in glass cell consisted three electrode first Cu specimen as working electrode (Cu coins was welded in glass rod with size larger than the specimen by epoxy resin in the space among glass rod and Cu), a reference electrode (SCE) and Pt wire as counter electrode (1 cm^2). The electrode potential was given for 30 min to stabilize before first tests. DILTIAZEM HYDROCHLORIDE PP plots were given by replacement the electrode potential from (-300 to +200 mV) against open circuit potential attendance of a scan rate of $1mVs^{-1}$. % IE and (θ) given as follow (2):

$$\%IE = 100 \times \theta = 100 \times [(I_{corr} - I_{corr(inh.)} / I_{corr}] \quad (2)$$

Where I_{corr} and $I_{corr(inh.)}$ are the lack and inhibited current corrosion density data, severally,. EIS tests were done in a range of frequency of 100 kHz to 10 mHzby5 mV amplitude peak-to-peak utilized ac signals at corrosion potential. The protection efficiency (% IE) and the (θ) of the utilized inhibitors given from the impedance tests can be measured by equation (3):

$$\%IE = 100 \times \theta = 100 \times [1- (R^\circ_{ct}/ R_{ct})] \quad (3)$$

Where R°_{ct} = the resistance without inhibitor and R_{ct}=the in presences of Diltiazem Hydrochloride inhibitor. EFM occurred by utilized2 frequencies first 2 Hz and second 5 Hz [29]. The outcome data were carried out with a Gamry apparatus Potentiostat /Galvanostat /ZRA, (PCI300/4) this contains a Gamry framework system depend on the ESA 400, applications of Gamry contain DC105 software for DC corrosion calculation, for EIS software EIS300 and EFM 140 software for calculation. Echem Analyst software was utilized for drawing, curves and fitting value. A computer was utilized for data summation.

2.4. Surface examinations

The surface Cu was readying by putting the coins for six hours in nitric acid attendance and lake of optimum concentration of Diltiazem Hydrochloride, after polished utilized various emery papers, washed by water bi-distilled then immerse it in the solution. After this time for immersion, the coins were washed, dried and measured by the spectrometer. The surfaces of Cu were tests by utilized an X-ray diffractometer Philips, a scanning electron (SEM, JOEL, JSM-T20, Japan).

2.5. Quantum calculations

All the quantum chemical tests were occurred with finishing geometry similarity utilized Accelrys Material Studio.

3. RESULTS AND DISCUSSION

3.1. WL tests

WL of Cu coins in 1 molar HNO_3, with and without of various doses of the Diltiazem Hydrochloride, were measured after three hours of dipping at 25^0C (Figure 1). Outcome data of % IE are obtained in Table 1. The presence of the Diltiazem Hydrochloride lowers the Cu corrosion rate (CR) in acidic medium. The %IE was improved by rise the doses of the Diltiazem Hydrochloride.

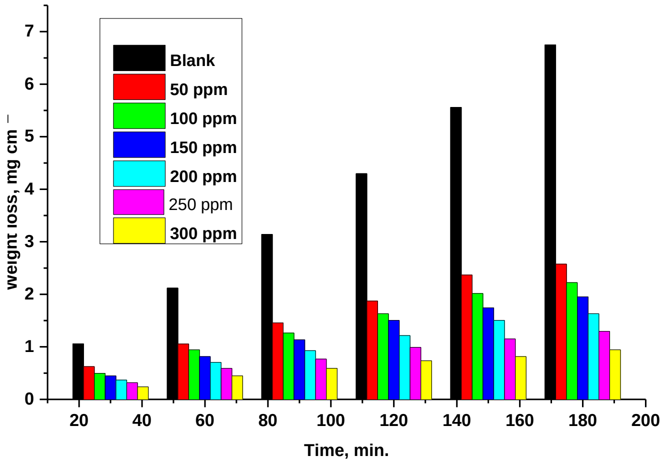


Figure 1. Time - WL diagram for Cu dissolution in 1M HNO_3 in nonexistence and existence of various doses of investigated Diltiazem Hydrochloride at 25^0 C

Table 1. IE of Diltiazem Hydrochloride at different doses as determined from WL method at 25 ^{0}C

Conc., ppm	C.R (mg cm^{-2}min^{-1})	%IE
------	0.0360	----
50	0.0110	71.0
100	0.0090	76.0
150	0.0080	79.5
200	0.0060	81.7
250	0.0050	83.9
300	0.0040	85.5

3.1.1 Temperature influence

The temperature effect on the protection among Cu reaction with acid is maximum complex, due to the changes carried out on the Cu surface, the rise corrosion rate by the temperature improve. The corrosion rate of Cu in 1M HNO_3 in nonexistence and existence of different doses of investigated Diltiazem Hydrochloride was research in the range of temperature of (25 – 45 ^{0}C) utilized by WL tests. The protection efficiency lower with temperature rising but at slower rate without Diltiazem Hydrochloride solutions with increasing the concentration of the inhibitor, as shown in Table 2, for Diltiazem Hydrochloride illustrates the adsorption decrease with increasing the temperature and corrosion rate (C.R.) , Indicating that the improve of temperature given the lower of the adsorption of Diltiazem Hydrochloride and then the dissolution process had acceleration so, the adsorption behavior of inhibitors on Cu surface in 1MHNO_3 occurs through physical adsorption. The decrease of protection efficiency with temperature increasing; the inhibitor is found adsorbed physically.

Table 2. IE of investigated Diltiazem Hydrochloride at different doses from WL measurements for Cu corrosion after120 min in 1M HNO_3 solution at different temperatures

Conc ppm	Temp. ^{0}C	C.R mgcm^{-2}min^{-1}	%IE
blank	30	0.056	----
	35	0.1010	----
	40	0.1350	----
	45	0.3240	----
50	30	0.0170	66.3
	35	0.0350	63.7
	40	0.0550	56.8
	45	0.1410	53.9
100	30	0.0160	71.8
	35	0.0310	68.7
	40	0.0480	62.3
	45	0.1290	59.0
150	30	0.0140	75.5

	35	0.0280	72.0
	40	0.0430	66.3
	45	0.1190	62.3
200	30	0.0120	78.0
	35	0.0240	74.4
	40	0.0370	69.1
	45	0.1060	64.7
250	30	0.0110	80.3
	35	0.0210	76.1
	40	0.0330	71.1
	45	0.0920	66.9
300	30	0.0080	82.0
	35	0.0190	77.8
	40	0.0300	72.5
	45	0.0840	68.1

3.1.2. Kinetic –thermodynamic corrosion parameters

The E^*_a of the corrosion reaction was measured utilized Arrhenius equation (4) [30].

$$k = A \exp(-E^*_a / RT) \qquad (4)$$

Where (A) = constant Arrhenius, (k) = corrosion rate, (T) = temperature absolute and (R) =constant gas. The values of E^*_a given from the lines slope of curves1/T vs.log k with and without doses of investigated Diltiazem Hydrochloride at different temperatures are recorded in Table 3.

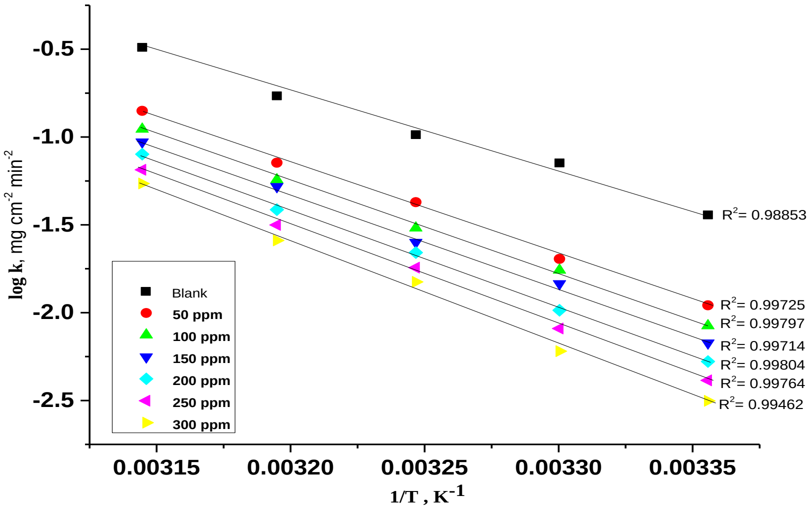


Figure 2. Arrhenius diagrams of variation of1/T against log k for the dissolution of Cu in 1M HNO_3 in nonexistence and existence various doses of investigated Diltiazem Hydrochloride

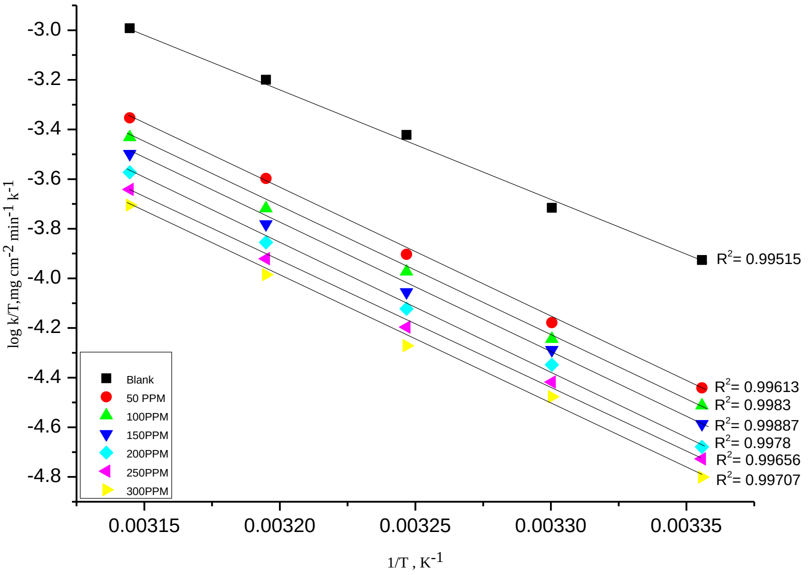


Figure 3. Plots of 1/ T vs log k / T for the dissolution of Cu in 1M HNO_3 without and with different doses of investigated Diltiazem Hydrochloride

Figure 2 given the linear regression (R^2) is close to 1 which led to the Cu corrosion in 1 M HNO_3 solution can be illustrated by utilized the kinetic model in Table 3. (E^*_a) shows larger data with the Diltiazem Hydrochloride than lack of it. Therefore, the Diltiazem Hydrochloride prevents the corrosion at slower temperature but this protection action is lower at maximum temperature. Also, improve in E^*_a with the appending of unlike doses of investigated Diltiazem Hydrochloride lead to that the rise energy barrier.

Table 3. Kinetic activation parameters for Cu in 1M HNO_3 in the absence and presence of different doses of Diltiazem Hydrochloride

Conc., ppm	E_a^* kJmol^{-1}	ΔH^* kJmol^{-1}	ΔS^* Jmol^{-1}K^{-1}
------	83.1	36.1	147.2
50	99.9	43.4	120.5
100	100.3	43.9	116.1
150	103.2	44.8	107.2
200	106.5	46.2	101.2
250	108.4	47.1	97.9
300	112.7	48.9	73.8

These data given that the presence of the Diltiazem Hydrochloride rise the E^*_a of the Cu dissolution reaction and that the process is diffusion controlled ($E_a^* > 39.9$ kJ mol^{-1}). The activation in the active sites were blocking by associated with rise in the E^*_a of corrosion of Cu in the inhibited state [31]. The E^*_a= 32 kJ mol^{-1}was recorded, this value is in best agreement with the work obtained by

Fouda et al [32] and others [33]. (Δ H*, ΔS*) are measured from transition state theory from the Eq. below (5) [33].

$k = TR/Nhe^{(\Delta S^*/R)} e^{(-\Delta H^*/ RT)}$ (5)

Where (N) =Avogadro’s number (h) =Planck’s constant. Figure 3 give a plot of (1/T) vs log (k /T). Straight lines are occurred with a slope=(ΔH*/2.303 R) and an intercept = (log R/Nh + ΔS*/2.303 R) from which the data of ΔS*and ΔH*are measured and recorded in Table 3.

Inspection of Table 3, it is clear that the positive values of ΔH* reflect that the adsorption process of the Diltiazem Hydrochloride on the surface of Cu is an endothermic process. Moreover the increase in the ΔH*attendance of the Diltiazem Hydrochloride means that the appending of Diltiazem Hydrochloride to 1 M HNO_3 solution rise the height of the energy barrier of the corrosion reaction to an extent depends on the dose of Diltiazem Hydrochloride. The adsorption of the Diltiazem Hydrochloride on the metal surface given a decrease number of hydrogen atoms adsorbed on it; this will cause a lower in evolution hydrogen rate rather than the rate of metal liquefaction, due to of the blocking of the Cu surface by adsorbed molecules of the Diltiazem Hydrochloride. The ΔS* data attendance and lack of the Diltiazem Hydrochloride are negative and maximum; this led to the activated complex in the rate-determining step prefer an association rather than liquefaction step, i.e. a lower in disordering obtain on going from reactants to the activated complex and the activated molecules were in maximum order state [34].

3.1.3. Adsorption isotherms

The most optimum ways of given adsorption quantitatively is by the adsorption isotherm [35]. The data (θ) were carried out at unlike doses of Diltiazem Hydrochloride in1 M HNO_3 solution. The best fitting data was isotherm Temkin by drawn log C versus (θ) for all Diltiazem Hydrochloride doses. Figure 4 a line straight all cases was occurred, this given that the adsorption of Diltiazem Hydrochloride on the surface of Cu obeys Temkin. The data of (ΔG°_{ads}) is connected with (K) equilibrium constant and (ΔG°_{ads}.) can be measured by the following equation [36].

$K_{ads} = 1/55.5 \exp [-\Delta G^{\circ}_{ads}/RT]$ (6)

These outcome data confirm the assumption that adsorbed Diltiazem Hydrochloride on Cu surface by the hetero atoms (lone pair of electrons). The (ΔG°_{ads}) and (K_{ads}) data for Diltiazem Hydrochloride were measured in Table 4These values were decrease with increasing temperature K_{25}> K_{30}>K_{35}>K_{40}>K_{45}. The high negative values of (ΔG°_{ads}) indicate that this compound is maximum adsorbed on Cu surface at all the temperature ranges occurred but the adsorption lower with the rise in temp (physisorption), the absolute data of ΔH^{o}_{ads} given in this study was decrease than (100 kJ mol^{-1}), given physisorption adsorption[37].

The –ve sign ΔG°_{ads} ensure that spontaneity of the adsorption. The maximum data of (K_{ads}) lead to the higher adsorption of Diltiazem Hydrochloride on Cu surface. This result reflects the raising capability, by formation structural on the Cu surface [38].

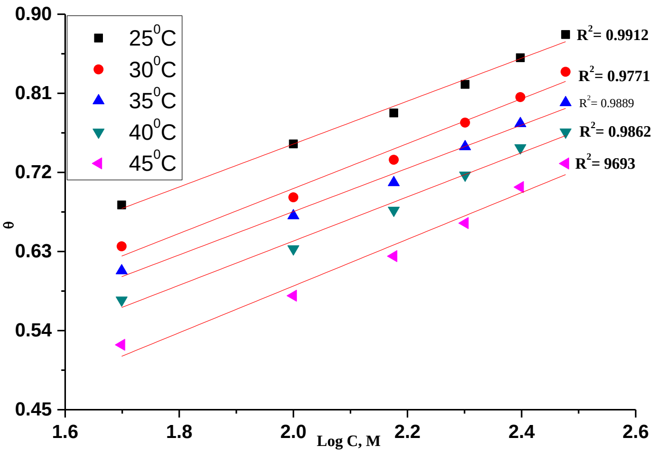


Figure 4. Temkin adsorption isotherm at various doses from the expired Diltiazem Hydrochloride at different temperatures for the Cu in 1M HNO_3 solution

Table 4. Adsorption parameters for Cu dissolution at various concentration of the expired Diltiazem Hydrochloride in 1 M HNO_3 at unlike temperatures

Temp. K	Log K_{ads}	-Δ G^o_{ads} kJ mol^{-1}	- Δ H^o_{ads} kJ mol^{-1}	- Δ S^o_{ads} J mol^{-1} K^{-1}
298	1.08	16.13	74.2	195.66
303	0.88	15.21		194.88
308	0.72	14.55		194.70
313	0.55	13.77		193.66
318	0.22	11.98		193.06

The measured data of (ΔG^o_{ads})are around (16-12) kJ mol^{-1} and the ΔH^o_{ads} given in this study = 74.2 kJ mol^{-1}, led to the mechanism of adsorption for Diltiazem Hydrochloride on Cu in 1M HNO_3 solution at the studied temperatures is physisorption.

3.2. Electro chemical measurements

3.2.1. PP tests

Theoretically, Cu can scarcely be corroded in the deoxygenated acid solutions, as Cu cannot replace hydrogen from acidic solutions [39]. Oxygen dissolved may be lower on Cu surface and corrosion occurred. The hydrogen evolution reaction ignores and only given oxygen reduction in the nitric acid solutions [40]. Nitric acid is a biggest Cu oxidizer capable of rapidly attacking Cu. In addition to, the PP diagrams prevent no slope steep in the anodic range, meaning that no passive films are obtain on the metal surface. PP test were obtain in order to give information for the kinetics of the anodic and cathodic reactions. Figure 5 give PP habit of Cu electrode in 1M HNO_3 attendance and lack of unlike doses of Diltiazem Hydrochloride . The data of PP were measured from the plots of Figure 5 and are recorded in Table 5for Diltiazem Hydrochloride .

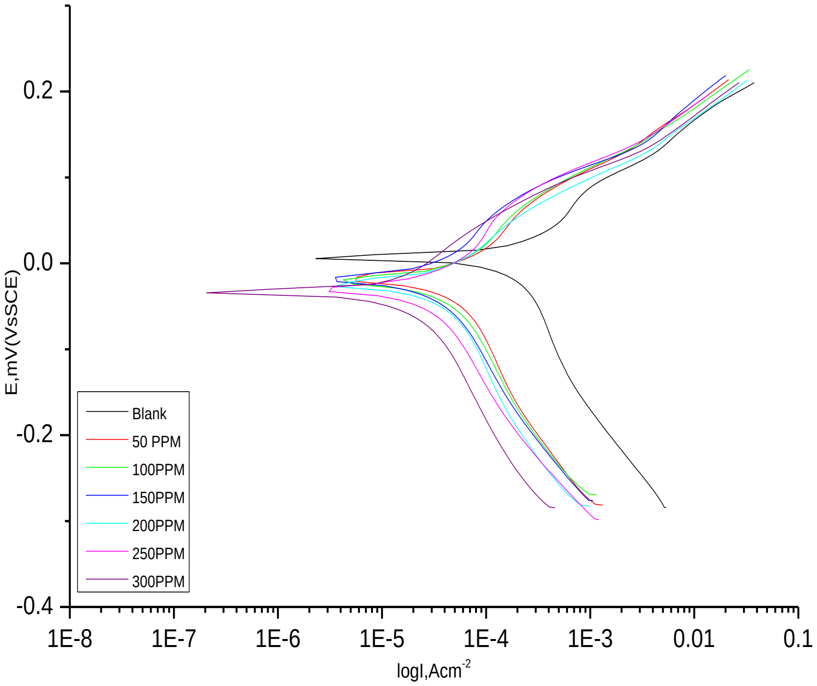


Figure 5. PP plots for the corrosion of Cu in 1M HNO_3without and with and without doses of investigated Diltiazem Hydrochloride at 25 ^{0}C

Table 5. Data from PP of Cu in 1M HNO_3attendance of unlike doses of expired Diltiazem Hydrochloride at 25^{0}C

Conc., ppm	-E_{corr} mVvs SCE	i_{corr} μA cm^{-2}	β_C mV dec^{-1}	β_a mV dec^{-1}	C.R mpy	Θ	%IE
Blank	43	208.0	234	100	200	-----	-----
50	22	171	190	103	95	0.178	17.8
100	20	85.4	240	140	44	0.589	58.9
150	14	76.7	222	121	39	0.631	63.1
200	30	70.80	220	198	36	0.660	66.0
250	25	56.1	256	101	29	0.730	73.0
300	19	49.9	209	118	22	0.76	76.0

The outcome data in Table 5 revealed that both the anodic and cathodic reactions are affected by the appending of Diltiazem Hydrochloride and the protection efficiency rise as the Diltiazem Hydrochloride dose rises, meaning that the appending of Diltiazem Hydrochloride reduce the anodic liquefaction of Cu and also prevent the cathodic reactions. In the attendance of Diltiazem Hydrochloride (E_{corr}) was enhanced with no definite trend, lead to that Diltiazem Hydrochloride act as mixed–kind inhibitor in 1 M HNO_3, forming an adsorbed layer among the metal/solution interface that lower the available anodic and cathodic sites. The corrosion current density lowers obviously after the appending of Diltiazem Hydrochloride in 1 M HNO_3 and (%IE) improve with raising the dose of Diltiazem Hydrochloride. (% IE) and the (θ) was measured from equation (2). As indicated from Table

5, i) the change in β_c data among the Diltiazem Hydrochloride -containing systems and the blank are maximum than that of β_a, which led to the Diltiazem Hydrochloride dominantly inhibit cathodic reactions, even though anodic liquefaction of Cu is also inhibited and ii) The (i_{corr}) data lower by the appending of Diltiazem Hydrochloride Thus, appending of this Diltiazem Hydrochloride lower the Cu liquefaction as well as, prevent the cathodic reaction. On other words, the inhibitor lowers the surface available area for anodic dissolution and O_2 reduction without affecting the mechanism of reaction.

3.2.2. EIS measurements

The data from Nyquist curves is carried out by utilized the circuit in Figure 6, in which R_s=resistance electrolyte, R_{ct}= resistance charge-transfer. The EIS value give the protection habit of inhibitor with other method; Bode plots Figure 7, show that the total EIS rises with improving dose of Diltiazem Hydrochloride (log Z vs. log f). However Bode plot (log f vs. phase) give a continuous rise in the phase angle shift, which could be correlated with improvement the inhibitor absorbance on surface of Cu., Nyquist diagram given for the Cu electrode at respective corrosion potentials after 30 min inundation in 1 M HNO_3without and with various doses of Diltiazem Hydrochloride as shown in Figure 8. These plots give single capacitive loop related to charge transfer of the corrosion process, and the loops diameters rise with improve of Diltiazem Hydrochloride doses.

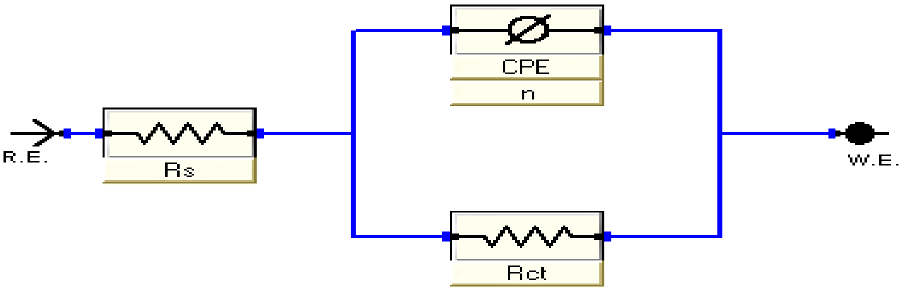


Figure 6. Equivalent circuit utilized to model impedance data in 1 M HNO_3 solutions

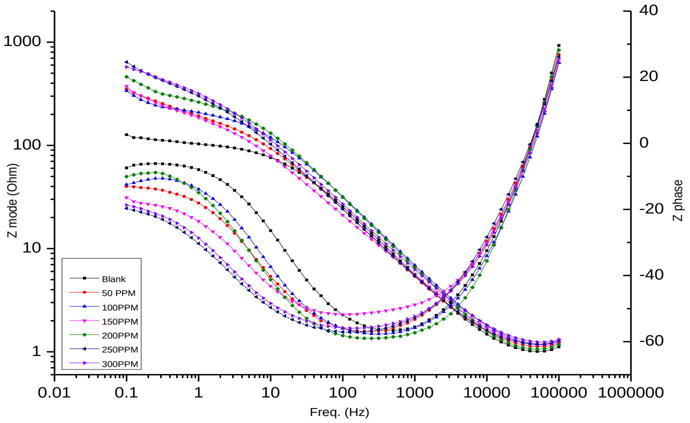


Figure 7. Bode curves for the Cu corrosion in1M HNO_3 in nonexistence and existence of doses of used Diltiazem Hydrochloride at 25°C

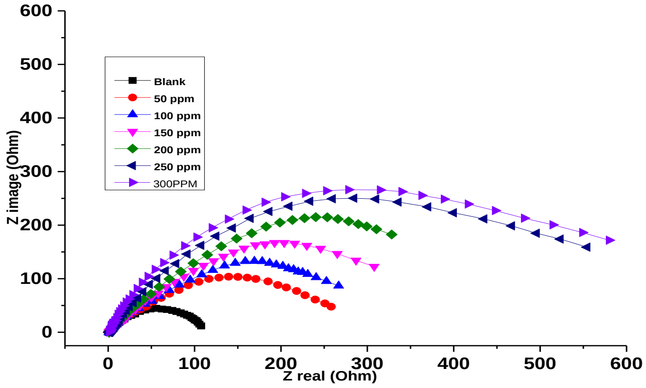


Figure 8. Nyquist diagram for the corrosion of Cu in 1M HNO_3 in nonexistence and existence of doses of used Diltiazem Hydrochloride at 25° C

Table 6. Kinetic parameter obtained from EIS tests for Cu in 1M HNO_3 in nonexistence and existence of doses of used Diltiazem Hydrochloride

Conc., ppm	R_s Ωcm^2	Y^0 $x10^{-6}$ $\Omega^{-1}s^n cm^{-2}$	n	R_p Ωcm^2	C_{dl} μFcm^{-2}	θ	%IE
Blank	0.927	773.1	0.756	109.4	348.0	-----	-----
50	0.985	454.4	0.704	261.4	185.5	0.582	58.2
100	1.041	276.4	0.732	286.2	100.8	0.618	61.8
150	0.977	851.6	0.490	300.8	206.7	0.636	63.6
200	0.933	259	0.791	324.9	178.6	0.663	66.3
250	1.256	512.3	0.691	557.1	140.0	0.804	80.4
300	1.057	472.0	0.162	580.0	60.0	0.811	81.1

It was known from the EIS valueTable6, that R_{ct} improve and C_{dl} lower with the raising of Diltiazem Hydrochloride doses. The improvement in (R_{ct}) data, and consequently of IE%, because the gradual movement of water molecules by the adsorption Diltiazem Hydrochloride molecules on the surface of Cu to obtain film adherent on the Cu surface. Also, this reduce of (C_{dl}) among the metal/solution interface with raising the Diltiazem Hydrochloride doses can result from a lower in local dielectric constant lead to the Diltiazem Hydrochloride was adsorbed on the Cu at both sites of anodic and cathodic [41].

3.2.3. EFM measurements

EFM is considered as non-destructive corrosion method which given quickly and directly the current corrosion results without information of PP, and with only a low polarizing signal. These EFM advantages make it an ideal for monitoring online corrosion [42].The great power of the EFM is the causality factors which give the validity and internal check for EFM calculation. The causality factors

CF-2 and CF-3 are measured from the frequency spectrum of the current responses. . Figure 9give the EFM of Cu in nitric acid solution with unlike doses of Diltiazem Hydrochloride at 25^{o} C.

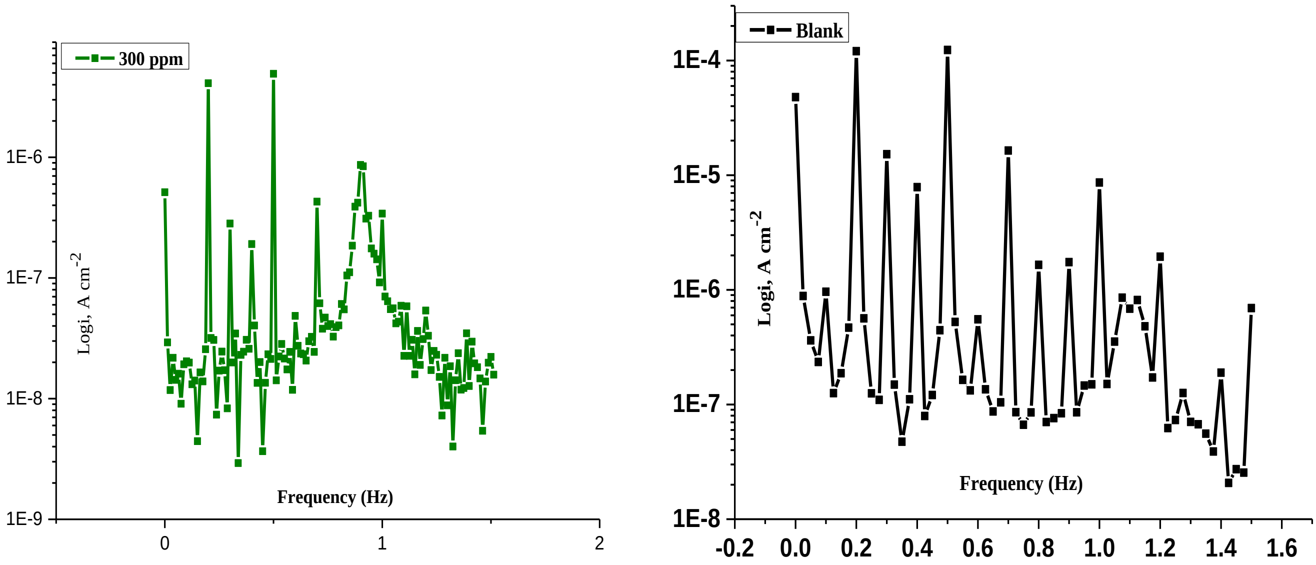


Figure 9. EFM spectra for Cu corrosion in 1M HNO_3 in nonexistence and existence of doses of Diltiazem Hydrochloride at 25^{o}C

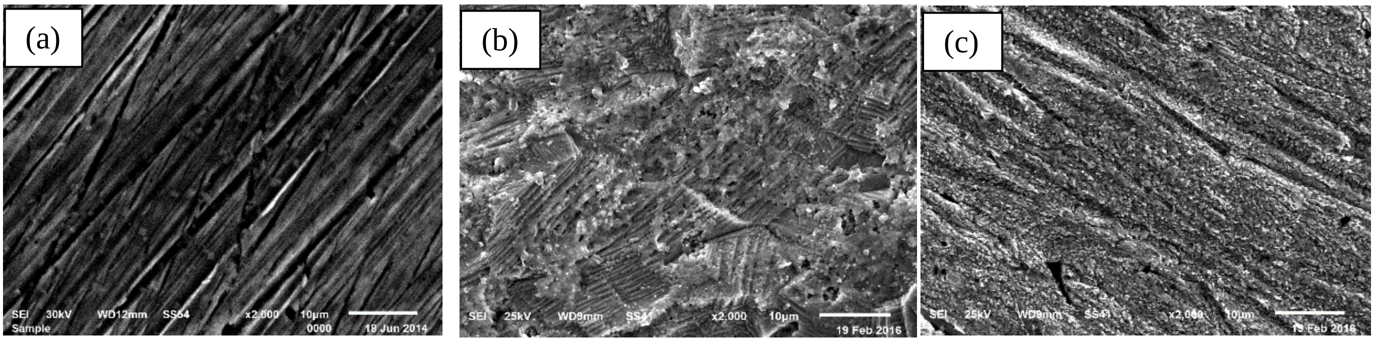
Table 7. Obtained Kinetic parameters of EFM tests for Cu in 1 M HNO_3 in nonexistence and existence of doses of used Diltiazem Hydrochloride

Con., ppm	i_{coor} μAcm^{2}	$β_a$ mV dec^{-1}	$β_C$ mVdec^{-1}	CF-2	CF-3	C. R mpy	Θ	%IE
Blank	265	90	323	1.92	2.53	135.70	----	----
50	82.85	84	209	1.75	2.98	42.44	0.687	68.7
100	70.25	72	163	1.81	2.38	35.98	0.735	73.5
150	62.23	66	158	1.80	2.10	31.88	0.765	76.5
200	54.31	79	181	1.87	2.30	27.82	0.795	79.5
250	45.14	69	154	1.76	3.34	23.13	0.830	83.0
300	34.96	58	144	1.86	2.44	17.91	0.868	86.8

CF-2 and CF-3, i_{corr}, and $β_c$ and $β_a$ were measured utilized larger peaks..These parameters were record in Table 7. The value in Table 7obviously give that, the appending of Diltiazem Hydrochloride at a given dose to the acidic solution lower(i_{corr}), lead to that Diltiazem Hydrochloride prevent the Cu corrosion. The (CF-2 and CF-3) given under unlike experimental are approximately equal to the theoretical values (2 and 3) led to the measured value are verified and of best quality. The % IE_{EFM} improves by raising the dose of Diltiazem Hydrochloride .

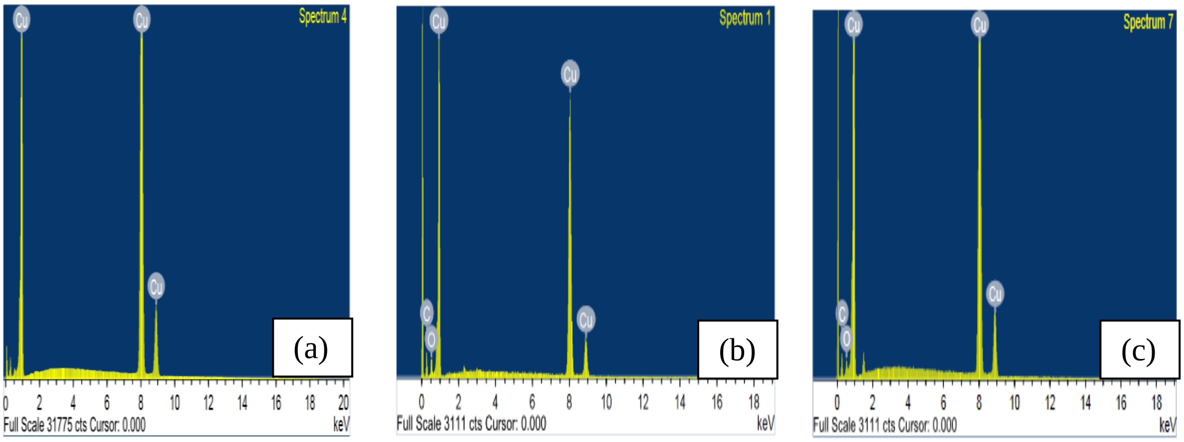
3.3. Surface Examinations

3.3.1. EDX and SEM tests



10 11 12

Figures (10a-c): SEM micrographs of surface of Cu Figure 10a, before of immersion in 1 M HNO_3 Figure 10b, after 8 hrs of dipping in 1 M $HNO_{3,}$ Figure 10c, after 8 hrs. of dipping in 1 M HNO_3+ 300 ppm of the used Diltiazem Hydrochloride at 25°C



Figures (11 a-c): EDX spectra of surface of Cu Figure (11a) before of dipping in 1 M HNO_3, Figure (11b) after 8 hrs. of dipping in 1 M HNO_3, Figure (11c) in 1 M HNO_3+ 300 ppm used Diltiazem Hydrochloride at 25 ^{0}C

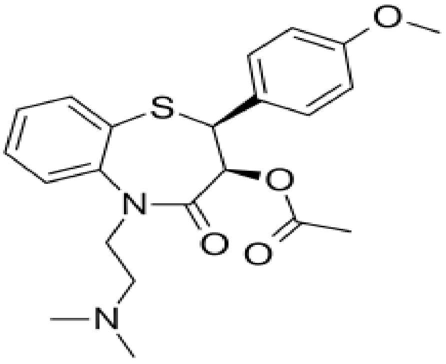
EDX & SEM tsts were occurred in order to verify if the Diltiazem Hydrochloride is adsorbed on surface of Cu or not. SEM images were indicative of the changes that accompany both corrosion and protection of the Cu Figures (10a-c). Figure 10a shows the free metal. Figure 10b shows the damage caused to the surface by nitric acid. Figure 10c gives SEM images of the Cu surface after treatment with 1 M HNO_3 containing 300 ppm of Diltiazem Hydrochloride . From these picture, the Cu surface seems to be almost unaffected by corrosion, due to Diltiazem Hydrochloride adsorption and give protective film on the surface of Cu. The corresponding EDX profile analyses are presented in Table 8 and Figures (11 a-c) EDX spectra with and without addition of 300 ppm of Diltiazem Hydrochloride . It is also important to notice the existence of Cu, C and O peaks in the EDX spectra of the Cu surface corresponding to the sample inundation for 8 hrs. in solutions with optimum dose of this Diltiazem Hydrochloride . The formation of a thin inhibitor film is the same with the SEM results.

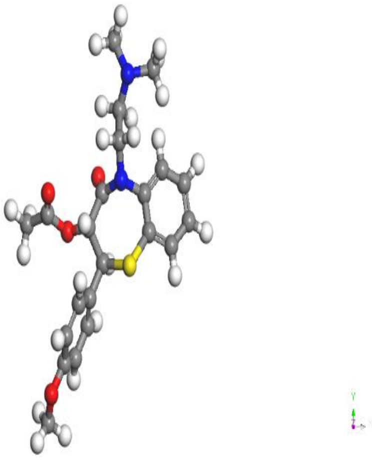
Table 8. Surface composition (weight %) of Cu after 8 hrs. of immersion in 1 M HNO_3+ 300 ppm Diltiazem Hydrochloride

Mass %	Cu	C	O
Pure	100	-	-
Blank	73.39	21.15	5.46
Diltiazem Hydrochloride	83.34	14.48	2.18

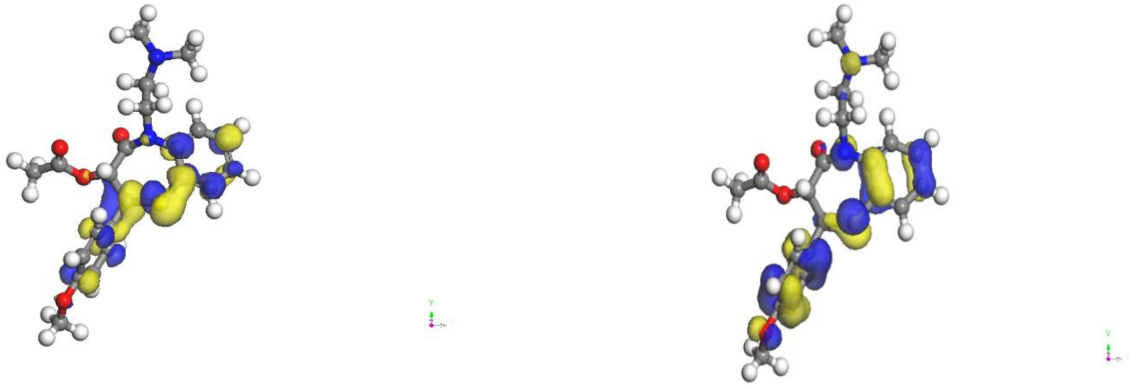
3.4. Quantum calculations

Figure 16 given the Mulliken charges and molecular orbital of Diltiazem Hydrochloride . Theoretical measurements were obtained for only the neutral forms, in order to give further insight into the experimental outcome. Data of quantum lead to such as (E_{HOMO} and E_{LUMO}), the obtain heat ΔH and energy gap ΔE, are measure by semi-empirical AM1, MNDO and PM3 tests has been obtain in Table 9. It has been done that the maximum, i.e decrease–ve E_{HOMO}, is associated of Diltiazem Hydrochloride inhibitor, the higher the trend of transpiring electrons to unoccupied d orbital of the Cu, and the greatest the corrosion protection, in appending, the reduce E_{LUMO}, the best to gain of electrons from Cu surface [45]. From Table 9, it is clear that ΔE given by the three techniques in case of Diltiazem Hydrochloride , which enhance the assumption that Diltiazem Hydrochloride molecule will be absorbed power on Cu surface, due to facilitating of electron transfer among molecular orbital HOMO and LUMO which occurred during its adsorption on the Cu surface and thereafter attendance the higher of IE.. Reportedly, good corrosion inhibitors are usually this pharmaceutical compound which do not only offer electrons to unoccupied orbital of the metal, but also gain free electrons from the Cu [46].The quantum parameters validate our results.





Mulliken charges



HOMO LUMO

Figure 16. Molecular orbital plots and Mulliken charges of the Diltiazem Hydrochloride

Table 9. The calculated quantum chemical parameters for the expired Diltiazem Hydrochloride

Comp.	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
Diltiazem Hydrochloride	-9.365	-0.978	8.387	4.194	0.238	-5.172	5.172	5.640

3.5. Inhibition of corrosion mechanism

Inhibition of the Cu in 1 M HNO_3 by the Diltiazem Hydrochloride as noted by WL , PP, and other methods were found to rely on the adsorption sites in the molecule and their charge densities, molecular size and stability of these additives in acidic medium. The corrosion protection is due to Diltiazem Hydrochloride adsorption among the interface of electrode/ solution, the adsorption of Diltiazem Hydrochloride relies on the metal nature and the adsorption mode of the Diltiazem Hydrochloride. It was concluded that the mode of adsorption rely on the metal affinity towards the S, O,N and π-electron clouds of the ring. Metals such as Cu, which have a higher attract towards aromatic moieties, were adsorb benzene rings in a flat orientation. The reasonable mechanism of the Diltiazem Hydrochloride inhibition of Cu corrosion may derived based on the adsorption on the Diltiazem Hydrochloride molecule exist as protonated via O, N and S atoms in acidic solution. The positively charged Diltiazem Hydrochloride molecule could be adsorbed to Cu surface with electrostatic interaction between the negatively charged NO_3^- and the protonated Diltiazem Hydrochloride molecule [45]. On the other hand, Diltiazem Hydrochloride molecules are adsorbed on Cu surface via an unshared pair of electrons present on the present heteroatom's [46]. The protonated Diltiazem

Hydrochloride molecules are also adsorbed onto the cathodic sites of the Cu and reduce the cathodic reactions.

5. CONCLUSIONS

The studied unused Diltiazem Hydrochloride is effective inhibitor for the dissolution of Cu in 1 M HNO_3 solution. This Diltiazem Hydrochloride retard corrosion by adsorption on Cu surface, and the Diltiazem Hydrochloride adsorbed on Cu follow Temkin isotherm. The PP research revealed that Diltiazem Hydrochloride play as mixed kind inhibitor in acidic medium. The outcome given from the four tests are in reasonably best agreement. The theoretical data support the results from experimental. The applied method given that this

References

1. K. F. Khaled, A.S. Fadl-Allah and B. Hammouti, *Mater. Chem. Phys.*, 117 (2009) 148.
2. M.M. El-Naggar, *Corros. Sci.*, 42(2000) 773.
3. Woo-Jin. Lee, *Mater. Sci. Eng. A.*, 348 (2003) 217.
4. S.A.Abd El-Maksoud, A.A. El-Shafei, H.A. Mostafa and A.S. Fouda, *Mater. Corros.*, 46(1995)468
5. S. Abd El-Waness, *Anti-Corros. Methods Mater.*, 41(1994) 3.
6. L.M. Madkour, M.A. Elmorsi and M. M. Ghoneim, *Monat. CHem.*, 126(1995)1087.
7. S.A. Abd El-Maksoud and H.H. Hassan, *Mater.Corros*., 58(2007)369.
8. A.S. Fouda, A. Abd El-Aal and A.B. Kandil, *Desalination*, 201(2006)216.
9. A.K. Maayta, M.B. Bitar and M.M. Al-Abdallah, *Br.Corros.* J., 36(2001)133.
10. M. Khodari, M.M. Abou-krisha, F.H. Assaf, F.M. El-Cheikh and A.A. Hussien, *Mater. Chem. Phys*., 71(2001)279.
11. G. Trabanelli, *Corrosion*, 47(1991)410.
12. F. Zucchi, G. Trabanelli and C. Monticelli, *Corros. Sci.*, 38(1996)147.
13. M. Ohsawa and W. Suetaka, *Corros. Sci.*, 19(1979)709.
14. V. Lakshminarayanan, R. Kannan and S.R. Rajagopalan, *J.Electroanal.Chem*. ,364(1994) 79.
15. I. Ignat, S. Varvara, L. Muresan, Studia Univ. Babes-Bolyai, *Chemia*, *L1* (2006) 127.
16. L. Ying, F. Hailtao, Z. Yifan and W. Wuji, *J.Mater. Sci*., 38(2003)407.
17. OrlinBlajiev, AnnickHubin, *Electrochim.Acta*, 49(2004)2761.
18. E.M. Sherif and Su-Moon Park, *Electrochim.Acta* ,51(2006)6556.
19. E. M. Sherif, *Appl.Surf.Sci.*, 252(2006) 8615.
20. E.M. Sherif and Su-Moon Park, *Corros.Sci. 48*(2006) 4065.
21. E.M. Sherif, A.M.Shamy, M.M.Ramla and A.O.H.ElNazhawy, *Mater.Chem. Phys.*, 102(2007) 231.
22. L. Valek and S. Martinez, *Mater.Lett.* , 61(2007)148.
23. S.A.Umeoren, O.Obobe, I.O.Igwe and E.E.Ebenso, *J.Appl.Poly.S*ci., 105(2007) 3363.
24. S.A.Umeoren, U.M.Eduok and E.E.Oguzie, *Port. Electrochim. Acta*, 26(6)(2004) 533.
25. E.E.Ebenso, *Electrochem*., 19(5)(2004) 209.
26. A.S.Fouda, E.M.Mabrouk and M.Y.El-Banawy, *J. Electrochem. Plating Technol.*, (2016) 1.
27. M.M.Motawea, H.S.Gadow and A. S. Fouda, Global *J. Res. Eng., 16(1) (2016) 7.*
28. R.W. Bosch, J. Hubrecht, W.F. Bogaerts and B.C. Syrett, Corrosion, 57(2001) 60.
29. G. Trabanelli, in "*Corrosion Mechanisms*" (Ed. F. Mansfeld) Marcel Dekker, New York, (1987) pages 119.
30. A.S. Fouda and A. B.Abd El-Aal, *Desalination*, 201(1-3) (2006) 216.

31. F.H. Asaf, M. Abou- Krisha, M. Khodari, F. EL-Cheihk, A. A. Hussien, *Mater.Chem.Phys*. 93 (2002) 1.
32. A. Fiala, A. Chibani, A. Darchen and A. Boulkamh, *Appl. Surf. Sci.*, (24) (2007) 9347.
33. M. K. Gomma and M. H. Wahdan, *Mater.Chem.Phys*. 39 (1995) 209.
34. E.Khamis, *Corrosion*, 46 (1990) 476.
35. I.K. Putilova, S.A. Balizen, Y.P. Barasanik, Metallic corrosion inhibitors, Pergamum Press, Oxford. (1960) 30.
36. A. S. Fouda, D. Mekkia and A. H. Badr, *J.Korean Chem. Soc*., 57(2) (2013) 264.
37. F. L. Laque and H. R. Gapson; Corrosion resistance of metals and alloys; 2nd ed., Reinhold Publishing Corporation, New York, (1963).
38. A. Muller, W. Stockel, Schumacher, *J. Electroanal. Chem*., 219(1) (1987) 311.
39. W.H. Smyrl, J.O.M. Bockris, B.E.Conway and E. Yeager, R.E. White (Eds.), Comprehensive Treatise of Electrochemistry, Plenum Press, N.Y., 4(1981) 116.
40. E. McCafferty and N Hackerman, *J. Electrochem.Soc*., 119 (1972) 146.
41. E.Kus and F. Mansfeld,*Corros.Sci.*,48(4)) (2006) 965.
42. R. R. Anand, R. M. Hurd and N. Hackerman, *J. Electrochem. Soc*., 112 (1965) 138
43. I. Lukovits, K. Palfi, E. Kalman, *Corrosion*, 53 (1997) 915.
44. P. Zhao, Q. Liang, Y. Li, *Appl. Surf*. Sci., 252 (2005) 1596.
45. A.Doner, R.Solmaz, M.Ozcan and C. Kaardas, *Corros. Sci.*, 53(2011)2902.
46. X. Wang, H.Yang,F.Wang, *Corros.Sci.*, 53(2011)113.

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