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RESEARCH ARTICLE

Corrosion Inhibitors Based on Antibiotic Derivatives for Protection of Carbon steel Corrosion in Hydrochloric Acid Solutions

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Abstract

Some antibiotic derivatives namely, neomycin sulphate and amoxicillin were investigated as corrosion inhibitors for carbon steel in 1 M HCl solutions. Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, electrochemical frequency modulation (EFM) and weight loss methods were used to study the inhibition action of carbon steel in 1 M HCl solutions at 30°C. Electrochemical results showed that these compounds are efficient inhibitors for carbon steel and the efficiency reached to 81 %. The inhibition efficiency increases with the inhibitor concentration. The adsorption of these compounds on carbon steel surface follows the Freundlich adsorption isotherm. Polarization curves indicate that investigated antibiotic derivatives are mixed-type inhibitors. The Kinetic parameters of corrosion processes were calculated and discussed. The chemical and electrochemical methods gave similar results. The surface morphology was tested using scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX)

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1. Introduction

Carbon steel has been extensively used under different conditions in petroleum industries [1]. Aqueous solutions of acids are among the most corrosive media and are widely used in industries for pickling, acid cleaning of boilers, descaling and oil well [2, 6]. The main problem concerning carbon steel applications is its relatively low corrosion resistance in acidic solution. Several methods used currently to reduce corrosion of carbon steel. One of such methods is the use of organic inhibitors [7- 17]. Effective inhibitors are heterocyclic compounds that have π bonds, heteroatoms such as sulphur, oxygen and nitrogen [18]. Compounds containing both nitrogen and chloro atoms can provide excellent inhibition, compared with compounds containing only nitrogen or chloro atom [19]. Heterocyclic compounds such as antibiotic (pharmaceutical drugs) can provide excellent inhibition. These molecules depends mainly on certain physical properties of the inhibitor molecules such as functional groups, steric factors, electron density at the donor atom and electronic structure of the molecules [20, 21]. A few researchers have been reported the use of antibacterial drugs as corrosion inhibitors because of presence of oxygen, nitrogen and sulphur in their structures as active centers, high solubility in water, high molecular size, non-toxic "environmentally friendly" corrosion inhibitors, important in biological reactions and drugs that can be easily produced and purified [22-29]. Regarding the adsorption of the inhibitor on the metal surface, two types of interactions are responsible. One is physical adsorption which involves electrostatic force between ionic charges or dipoles of the adsorbed species and electric charge at metal/solution interface. Other is chemical adsorption, which involves charge sharing or charge transfer from inhibitor

molecules to the metal surface to form coordinated types of bonds [30]. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, and temperature.

In the present work, the inhibition characteristics of neomycin sulphate and amoxicillin were investigated as corrosion inhibitors for carbon steel in 1 M HCl solution using chemical and electrochemical techniques.

2. Experimental

2.1. Chemicals and materials

Hydrochloric acid (37 %), ethyl alcohol and dimethyl formamide (DMF) were purchased from Al-Gomhoria Company, Egypt, neomycin sulphate and amoxicillin were purchased from Shanghai Fine Chemicals Co., Ltd., Mainland, China with purity 99.5% and used without further purification. The molecular structures and other details of these compounds are given in Table (1). Double distilled water was used throughout all the experiments. The composition of carbon steel (weight %) is given in Table (2).

Table (1): Molecular structures, formulas and molecular weights of investigated compounds.

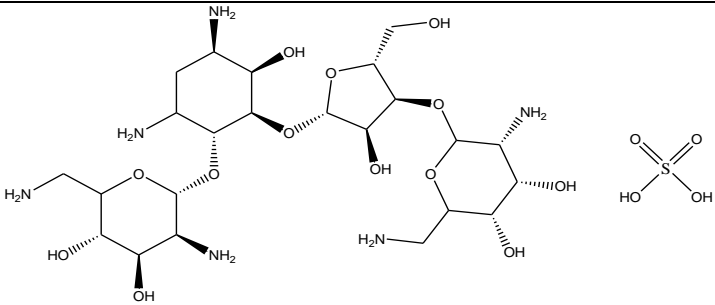
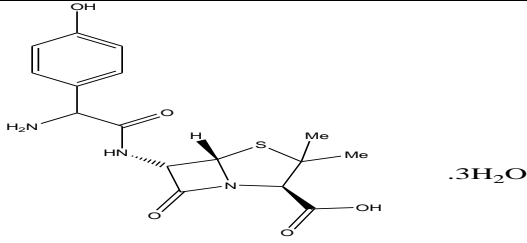
Inhibitors	Structures	Mol. Formulas & Mol. Weights
Neomycin sulphate		$C_{23}H_{48}N_6O_{17}S$ 712.72
Amoxicillin trihydrates		$C_{16}H_{25}N_3O_8S$ 419.45

Table (2): Chemical composition of carbon steel (weight %).

Element	C	Mn	P	Si	Fe
Weight (%)	0.200	0.350	0.024	0.003	rest

2.2. Methods

2.2.1. Weight loss measurements

Rectangular specimens of carbon steel with dimensions 2 x 2 x 0.2 cm were abraded with different grades of emery papers, degreased with acetone, rinsed with double distilled water and dried between filter papers. After weighting accurately, the specimens were immersed in 100 ml of 1 M HCl with and without different concentrations of inhibitors. After different immersion periods (each of 30 min till 180 min), the carbon steel samples were taken out, washed with double distilled water, dried and weighted again. The weight loss values are used to calculate the corrosion rate (R) in mmy^{-1} by Eq. (1):

$$R = (\text{weight loss in gram} \times 8.0) / DA t \quad (1)$$

Where D is carbon steel density in g cm^{-3} , A is exposed area in cm^2 , t is exposure time in hr.

The inhibition efficiency (% Y_w) and the degree of surface coverage (θ) were calculated from Eq. (2):

$$\%Y_w = \theta \times 100 = [(R^* - R) / R^*] \times 100 \quad (2)$$

where R^* and R are the corrosion rates of carbon steel in the absence and in the presence of inhibitor, respectively.

2.2.2. Electrochemical measurements

Electrochemical measurements were conducted in a conventional three electrodes thermostated cell assembly using Gamry Potentiostat/Galvanostat/ZRA (model PCI300/4). A platinum foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The carbon steel electrodes were 1 cm² and were welded from one side to a copper wire used for electrical connection. The electrodes were abraded, degreased and rinsed as described in weight loss measurements. All experiments were carried out at temperature (30 ± 1 °C). The potentiodynamic curves were recorded from -500 to 500 mV at a scan rate 1 mV s⁻¹ after the steady state is reached (30 min) and the open circuit potential (OCP) was noted. DC105 software was used for polarization measurements. The % Y_p and degree of surface coverage were calculated from Eq. (3):

$$Y_p\% = \theta \times 100 = [1 - (i_{\text{corr}}^0 / i_{\text{corr}})] \times 100 \quad (3)$$

where i_{corr}^0 and i_{corr} are the corrosion current densities of inhibited and uninhibited solutions, respectively.

Electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) experiments were carried out using the same instrument as before with a Gamry framework system based on ESA400. Gamry applications include software EIS300 for EIS measurements and EFM140 for EFM measurements; computer was used for collecting data. Echem Analyst 5.5 Software was used for plotting, graphing and fitting data. EIS measurements were carried out in a frequency range of 100 kHz to 10 mHz with amplitude of 5 mV peak-to-peak using ac signals at respective corrosion potential. EFM carried out using two frequencies 2 and 5 Hz. The base frequency was 1 Hz. In this study, we use a perturbation signal with amplitude of 10 mV for both perturbation frequencies of 2 and 5 Hz.

2. 2. 3. SEM-EDX Measurement

The carbon steel surface was prepared by keeping the specimens for 3 days immersion in 1 M HCl in the presence and absence of optimum concentrations of investigated derivatives, after abraded using different emery papers up to 1200 grit size. Then, after this immersion time, the specimens were washed gently with distilled water, carefully dried and mounted into the spectrometer without any further treatment. The corroded carbon steel surfaces were examined using an X-ray diffractometer Philips (pw-1390) with Cu-tube (Cu Ka1, $\lambda = 1.54051 \text{ \AA}$), a scanning electron microscope (SEM, JOEL, JSM-T20, Japan).

3. Results and discussion

3.1. Weight loss measurements

Figure (1) shows the weight loss–time curves for the corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of neomycin sulphate. Similar curves for amoxicillin were obtained and are not shown. The data of Table (3) show that, the inhibition efficiency increases with increase in inhibitor concentration from 1 x 10⁻⁶ to 15 x 10⁻⁶ M. The maximum inhibition efficiency was achieved at 15 x 10⁻⁶ M. The lowest inhibition efficiency (% Y_w) is obtained in the presence of amoxicillin, therefore % Y_w tends to decrease in the following order: neomycin sulphate > amoxicillin.

Table (3): Data of weight loss measurements for carbon in 1 M HCl solution in the absence and presence of different concentrations of investigated compounds at 30 °C.

Compound	Conc., x 10 ⁶ M	Corrosion rate, (CR) (mg cm ⁻² min ⁻¹)	θ	% Y_w
Blank	0.0	0.024	-	-
Neomycin sulphate	5	0.008	0.685	68.5
	7	0.007	0.72	72.0
	9	0.006	0.752	75.2
	11	0.005	0.79	79

	13	0.004	0.832	83.2
	15	0.003	0.879	87.9
Amoxicillin	5	0.009	0.614	61.4
	7	0.008	0.659	65.9
	9	0.007	0.685	68.5
	11	0.006	0.727	72.7
	13	0.005	0.767	76.7
	15	0.004	0.816	81.6

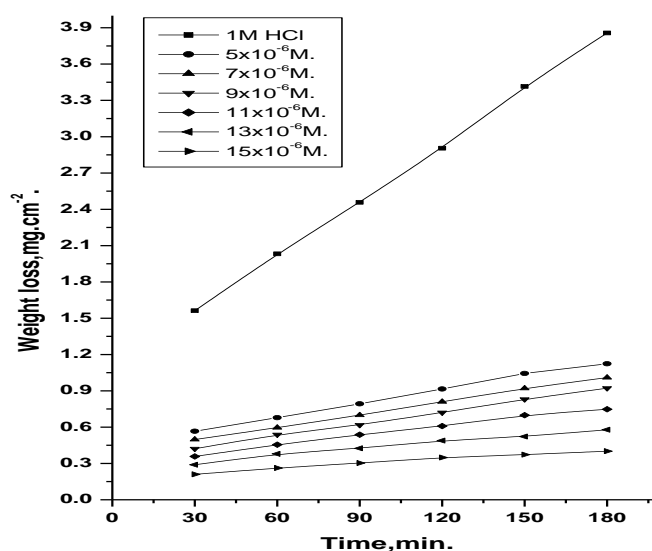


Figure (1): Weight loss-time curves for carbon steel dissolution in 1M HCl in the absence and presence of different concentrations of neomycin sulphate at 30°C.

3.2. Electrochemical measurements

3.2.1. Potentiodynamic polarization measurements

The potentiodynamic curves for carbon steel in 1 M HCl in the absence and presence of neomycin sulphate are shown in Fig. (2). Similar curves were obtained for amoxicillin (not shown). It is clear that; the investigated inhibitors affect the promoting retardation of anodic dissolution of carbon steel and cathodic hydrogen discharge reactions. Electrochemical parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel constants (β_a and β_c), degree of surface coverage (θ) and inhibition efficiency ($\%Y_p$) were calculated from Tafel plots and are given in Table (4). It is observed that the presence of inhibitor lowers i_{corr} values. Maximum decrease in i_{corr} values was observed for neomycin sulphate indicating that this is the most effective corrosion inhibitor. It is also observed from Table (4) the Tafel slopes do not change significantly in inhibited solution as compared to uninhibited solution. The investigated compounds do not shift the E_{corr} values significantly, suggesting that they behave as mixed type inhibitors [31]. Both cathodic (β_c) and anodic Tafel lines (β_a) are parallel and are shifted to more negative and positive direction, respectively by adding inhibitors. This is indicating that the mechanism of the corrosion reaction does not change and the corrosion reaction is inhibited by simple adsorption mode [32]. The irregular trends of β_a and β_c values indicate the involvement of more than one type of species adsorbed on the metal surface. The order of inhibition efficiency was found to be: neomycin sulphate > amoxicillin

3.2.2. Electrochemical impedance spectroscopy

The EIS provides important mechanistic and kinetic information for an electrochemical system under investigation. Nyquist impedance plots obtained for the carbon steel electrode at respective corrosion potentials after 30 min

Table (4): The effect of concentration of the investigated compounds on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), inhibition efficiency (Y_p %), and degree of surface coverage for the corrosion of carbon steel in 1 M HCl at 30 °C.

Concentration, M		i_{corr} , mA cm ⁻²	$-E_{corr}$, mV vs.SCE	β_a , mV dec ⁻¹	β_c , mV dec ⁻¹	θ	% Y_p
1 M HCl		1.1	459	106.8	151.7	-	-
Neomycin sulphate	5 x 10 ⁻⁶	0.473	445	115.5	98.1	0.57	57.0
	7 x 10 ⁻⁶	0.309	522	215.4	108.1	0.719	71.9
	9 x 10 ⁻⁶	0.255	523	202.3	74.2	0.768	76.8
	11 x 10 ⁻⁶	0.237	467	155	144.6	0.784	78.4
	13 x 10 ⁻⁶	0.214	503	171.6	100.6	0.805	80.5
	15 x 10 ⁻⁶	0.122	363	109.8	272	0.889	88.9
Amoxicillin	5 x 10 ⁻⁶	0.513	558	203.4	148.1	0.534	53.4
	7 x 10 ⁻⁶	0.483	465	120.8	122.6	0.56	56.0
	9 x 10 ⁻⁶	0.378	462	111.2	110.8	0.656	65.6
	11 x 10 ⁻⁶	0.270	455	115.5	110.2	0.754	75.4
	13 x 10 ⁻⁶	0.190	445	115.2	98.1	0.827	82.7
	15 x 10 ⁻⁶	0.170	442	118.8	90.2	0.845	84.5

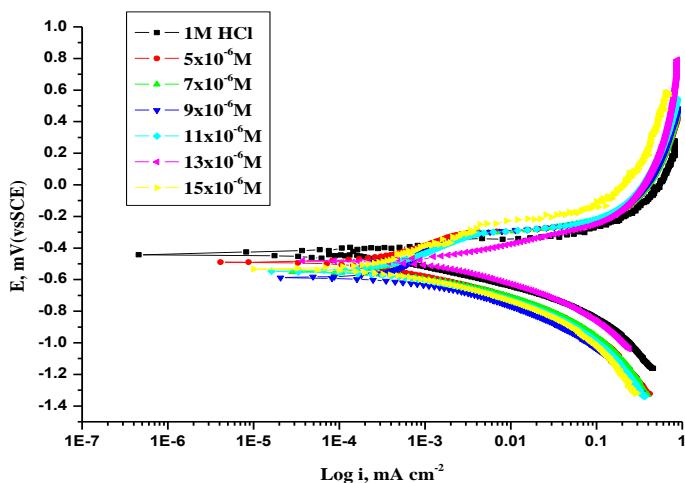


Figure (2): Potentiodynamic polarization curves for the corrosion of carbon steel in 1 M HCl in the absence and presence of various concentrations of neomycin sulphate at 30°C.

immersion in 1M HCl in presence and absence of various concentrations of neomycin sulphate is shown in Figure 3 (amoxicillin curves not shown). This diagram exhibits a single semi-circle shifted along the real impedance (Z_r). The Nyquist plots of neomycin sulphate do not yield perfect semicircles as expected from the theory of EIS, the impedance loops measured are depressed semi-circles with their centers below the real axis, where the kind of phenomenon is known as the ‘‘dispersing effect’’ as a result of frequency dispersion [33] and mass transport resistant [34] as well as electrode surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [35-39], etc. so one constant phase element (CPE) is substituted for the capacitive element, to explain the depression of the capacitance semi-circle, to give a more accurate fit. Impedance data are analyzed using the circuit in Figure (4); in which R_s represents the electrolyte resistance, R_{ct} represents the charge-transfer resistance and the constant phase element (CPE). According to Hsu and Mansfield [40] the correction of capacity to its real values is calculated from Eq. (6):

$$C_{dl} = Y_o (\omega_{max})^{n-1} \tag{6}$$

Where Y_o is the CPE coefficient, ω_{max} is the frequency at which the imaginary part of impedance ($-Z_i$) has a maximum and n is the CPE exponent (phase shift).

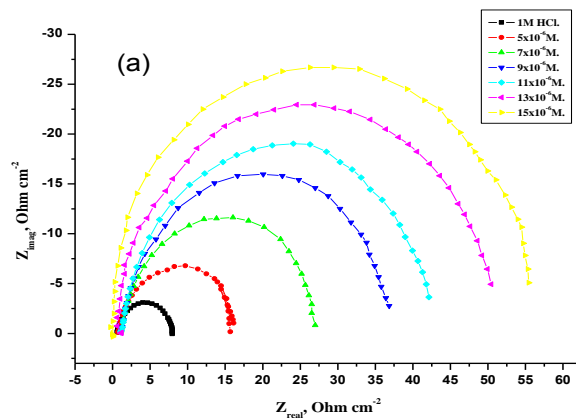


Figure (3): The Nyquist (a) and Bode (b) plots for corrosion of carbon steel in 1M HCl in the absence and presence of different concentrations of neomycin sulphate at 30°C.

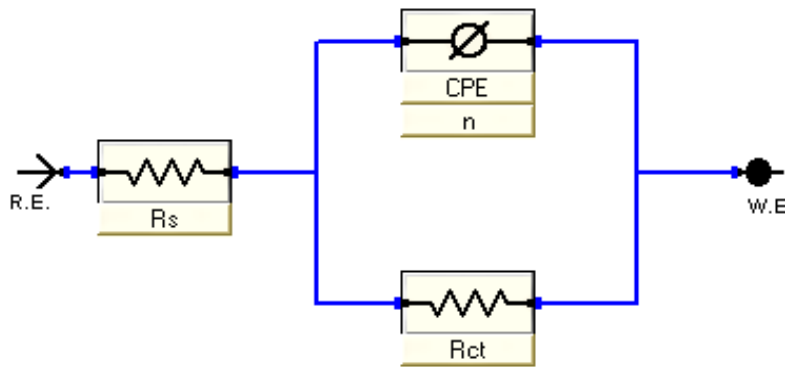


Figure (4): Equivalent circuit model used to fit the impedance spectra data.

The data obtained from fitted spectra are listed in Table (5). The $Y_I\%$ was calculated from Eq. (7):

$$Y_I \% = \frac{R_{ct} - R_{ct}^*}{R_{ct}} \times 100 \tag{7}$$

Where R_{ct} and R_{ct}^* are the charge-transfer resistances with and without the inhibitors, respectively.

Data in Table (5) show that; the R_s values are very small compared to the R_{ct} values. Also; the R_{ct} values increase and the calculated C_{dl} values decrease by increasing the inhibitor concentrations, which causes an increase of θ and Y_1 . The high R_{ct} values are generally associated with slower corroding system [41]. The decrease in the C_{dl} suggests that inhibitors function by adsorption at the metal/solution interface [42].

The inhibition efficiencies, calculated from EIS results, show the same trend as those obtained from polarization measurements. The difference of inhibition efficiency from two methods may be attributed to the different surface status of the electrode in two measurements. EIS were performed at the rest potential, while in polarization measurements the electrode potential was polarized to high over potential, non-uniform current distributions, resulted from cell geometry, solution conductivity, counter and reference electrode placement, etc., will lead to the difference between the electrode area actually undergoing polarization and the total area [43].

Table (5): Electrochemical kinetic parameters obtained by EIS technique for in 1 M HCl without and with various concentrations of investigated compounds at 30 °C.

Comp.	Conc., M .	R_s , $\Omega \text{ cm}^2$	$Y_{0_1} \times 10^{-3}$ $\mu\Omega^{-1} \text{ sn} * 10^{-6}$	n	R_{ct} , $\Omega \text{ cm}^2$	C_{dl} μFcm^{-2} $* 10^{-4}$	%IE
Neomycin sulphate	Blank	2.65	375.8	0.890	33	2.9	-----
	5x 10-6	1.22	235.4	0.774	102.8	0.156	67.9
	7 x 10-6	1.21	129.6	0.799	112.9	0.155	70.7
	9 x 10-6	0.753	176.1	0.708	120	0.808	72.5
	11 x 10-6	0.776	235.4	0.774	140	0.919	76.4
	13 x 10-6	0.739	383.3	0.703	159.5	0.311	79.3
	15x 10-6	0.660	523.9	0.779	180	0.491	81.7
Amoxicillin	5x 10-6	1.883	362.6	0.773	78.6	3.72	58.0
	7 x 10-6	1.85	241.9	0.891	89.7	1.85	63.2
	9 x 10-6	1.77	104.2	0.707	101	3.72	67.3
	11 x 10-6	1.66	468.5	0.794	125	2.25	73.6
	13 x 10-6	1.19	676.2	0.767	132.1	3.25	75.0
	15x 10-6	0.856	664.6	0.745	160.6	3.09	79.4

3.2.3. Adsorption isotherm

One of the most convenient ways of expressing adsorption quantitatively is by deriving the adsorption isotherm that characterizes the metal/inhibitor/ environment system [44]. The surface coverage (θ) values were tested graphically to allow fitting of a suitable adsorption isotherm. The plot of $\log \theta$ versus $\log C$ [Fig. (5)] yielded straight line curve clearly proving that the adsorption of these inhibitors from 1 M HCl solution on carbon steel surface obeys Freundlich adsorption isotherm:

$$\log \theta = \log K_{ads} + n \log C \quad (9)$$

Where K_{ads} is the adsorption equilibrium constant, n is the interaction parameter and C is the inhibitor concentration.

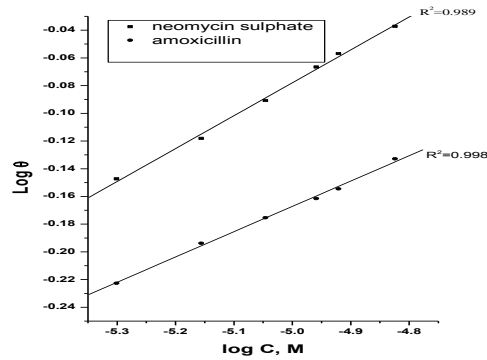


Figure (5): Curve fitting of corrosion data for carbon steel in 1M HCl in presence of different concentrations of organic additives to the Freundlich isotherm at 30°C.

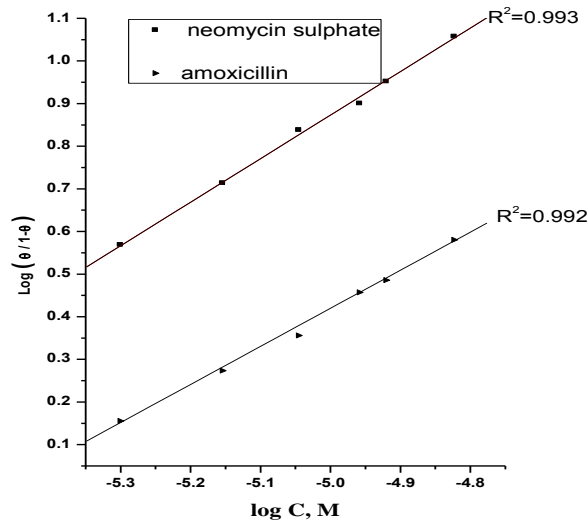


Figure (6): Curve fitting of corrosion data for carbon steel in 1M HCl in presence of different concentrations of inhibitors to the kinetic model at 30°C

kinetic-thermodynamic model evaluate theoretically the values of inhibitor equilibrium constant (K), free energy of adsorption (ΔG°_{ads}), number of active sites ($1/y$).kinetic model show the relation between $\log (\theta/1-\theta)$ vs. $\log C$ gives straight line Fig. (6), from its slope, y can be computed and from its intercept equilibrium constant (K) can be computed, then ΔG°_{ads} can be calculated (Table 6) from the following equation:

$$K = 1/ 55.5 \exp (-\Delta G^{\circ}_{ads}/ RT) \tag{10}$$

Table (6): Equilibrium constant (K), free energy of adsorption (ΔG°_{ads}), number of active sites ($1/y$) and the interaction parameter (n) for inhibitors at 30°C.

Inhibitors	Kinetic model	Freundlich model

	1/y	K	$-\Delta G_{ads}^{\circ}$, kJ mol ⁻¹	n	K	$-\Delta G_{ads}^{\circ}$, kJ mol ⁻¹
Neomycin sulphate	15.4	4.2	20.6	0.24	12.85	16.6
Amoxicillin	10.9	3.5	16.7	0.18	5.57	14.4

3.2.4- Kinetic parameters

The effect of temperature (30 – 60°C) on the performance of the inhibitors at different concentrations of (5× 10⁻⁶- 15× 10⁻⁶ M) for carbon steel in 1M HCl was studied using weight-loss measurements. Plot of log k (corrosion rate) against 1/ T (absolute temperature) Figures (7&9) for carbon steel in 1M HCl, gave straight lines for neomycin sulphate and amoxicillin, respectively. The values of the slopes obtained at different temperatures permit the calculation of Arrhenius activation energy (E_a^{*}). Kinetic parameters for corrosion of carbon steel were calculated from Arrhenius – type plot.

$$k = A \exp (-E_a^* / RT) \tag{11}$$

and transition state- type equation :

$$k = RT / Nh \exp (\Delta S^*/R) \exp (-\Delta H^* / RT) \tag{12}$$

The relation between log k / T vs. 1 / T gives straight line, from its slope, ΔH^{*} can be computed and from its intercept ΔS^{*} can be also computed Figures (8&10) for neomycin sulphate and amoxicillin respectively.

Table (7) exhibits the values of apparent activation energy E_a^{*}, enthalpies ΔH^{*} and entropies ΔS^{*} for carbon steel dissolution in 1M HCl solution. The presence of antibiotic derivatives increases the activation energies of carbon steel indicating strong adsorption of the antibiotic molecules on the metal surface and the presence of these additives induces energy barrier for the corrosion reaction and this barrier increases with increasing the additive concentrations.

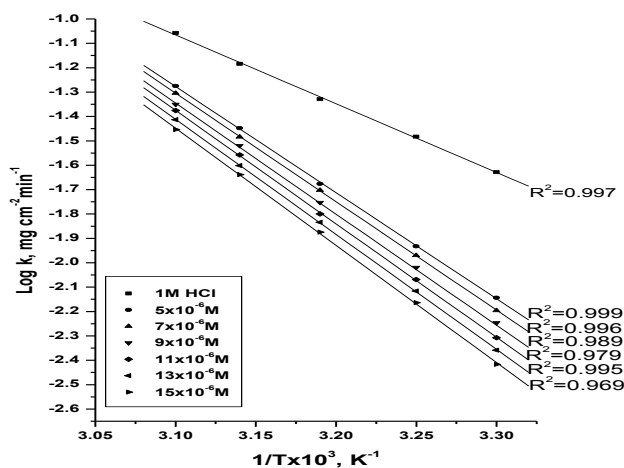


Figure (7): log k (corrosion rate) - 1/T curves for carbon steel dissolution in 1M HCl in the absence and presence of different concentrations of neomycin sulphate.

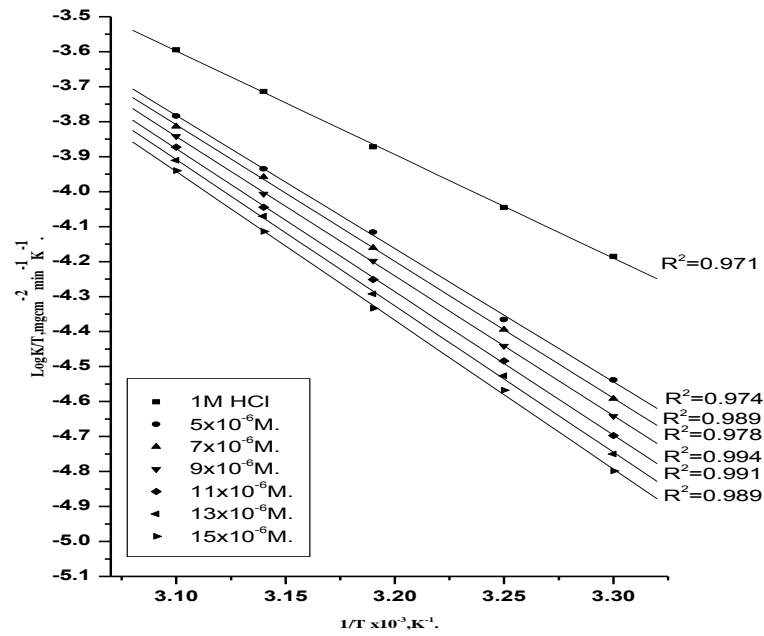


Figure (8): log (corrosion rate/T) - (1/T) curves for carbon steel dissolution in 1M HCl in the absence and presence of different concentrations of neomycin sulphate.

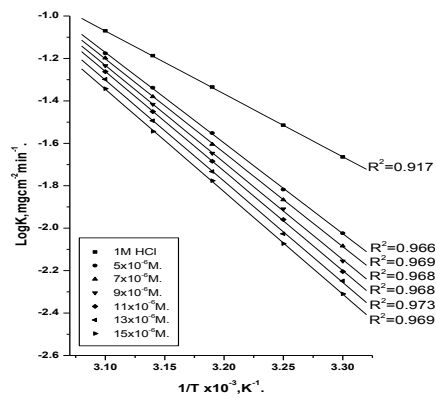


Figure (9): log k (corrosion rate) - 1/T curves for carbon steel dissolution in 1M HCl in the absence and presence of different concentrations of amoxicillin

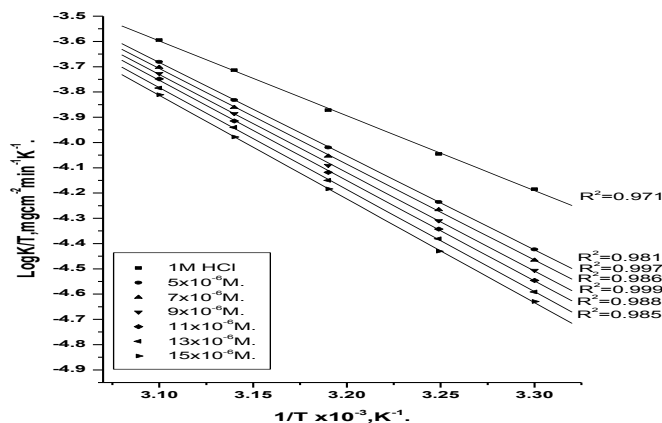


Figure (10): log (corrosion rate/T) - (1/T) curves for carbon steel dissolution in 1M HCl in the absence and presence of different concentrations of amoxicillin.

Table (7): Kinetic parameters for the dissolution of carbon steel in presence and absence of different concentrations of inhibitors in 1M HCl.

Inhibitor	Conc., M.	Activation parameters		
		E_a^*	ΔH^*	$-\Delta S^*$
		kJ mol^{-1}	kJ mol^{-1}	$\text{J mol}^{-1} \text{K}^{-1}$
Free Acid (1 M HCl)	0	56.7	53.9	50.6
Neomycin sulphate	5×10^{-6}	83.2	72.8	44.2
	7×10^{-6}	85.1	74.7	39.6
	9×10^{-6}	88.3	76.4	34.4
	11×10^{-6}	90.5	78.3	29.0
	13×10^{-6}	91.8	80.0	24.3
	15×10^{-6}	93.1	81.3	20.9
Amoxicillin	5×10^{-6}	81.6	70.9	47.9
	7×10^{-6}	84.0	72.5	43.6
	9×10^{-6}	86.2	74.5	38.1
	11×10^{-6}	88.1	75.9	33.8
	13×10^{-6}	89.9	77.3	30.2
	15×10^{-6}	91.9	78.5	27.0

3.2.5. – Scanning electron microscopy (SEM) studies

Figure (11) represents the micrograph obtained for carbon steel samples in presence and in absence of 15×10^{-6} M antibiotic derivatives after exposure for 3 days immersion. It is clear that carbon steel surfaces suffer from severe corrosion attack in the blank sample. It is important to stress out that when the compound is present in the solution, the morphology of carbon steel surfaces is quite different from the previous one, and the specimen surfaces were smoother. We noted the formation of a film which is distributed in a random way on the whole surface of the carbon steel. This may be interpreted as due to the adsorption of the antibiotic derivatives on the carbon steel surface incorporating into the passive film in order to block the active site present on the carbon steel surface. Or due to the involvement of inhibitor molecules in the interaction with the reaction sites of carbon steel surface, resulting in a decrease in the contact between carbon steel and the aggressive medium and sequentially exhibited excellent inhibition effect [45, 46].

3.2.6. Energy dispersion spectroscopy (EDX) studies

The EDX spectra were used to determine the elements present on the surface of C-steel and after 3 days of exposure to the uninhibited and inhibited 1 M HCl. Fig.12 shows the EDX analysis result on the composition of C-steel only

without the acid and inhibitor treatment. The EDX analysis indicates that only Fe and oxygen were detected, which shows that the passive film contained only Fe₂O₃.

Figure 12 portrays the EDX analysis of C-steel in 1M HCl only and in the presence of 15x10⁻⁶ M of pharmaceutical compounds. The spectra show additional lines, demonstrating the existence of C (owing to the carbon atoms of pharmaceutical compounds). These data shows that the carbon and O materials covered the specimen surface. This layer is entirely owing to the inhibitor, because the carbon and O signals are absent on the specimen surface exposed to uninhibited HCl. It is seen that, in addition to O, S, and C were present in the spectra. A comparable elemental distribution is shown in Table (8).

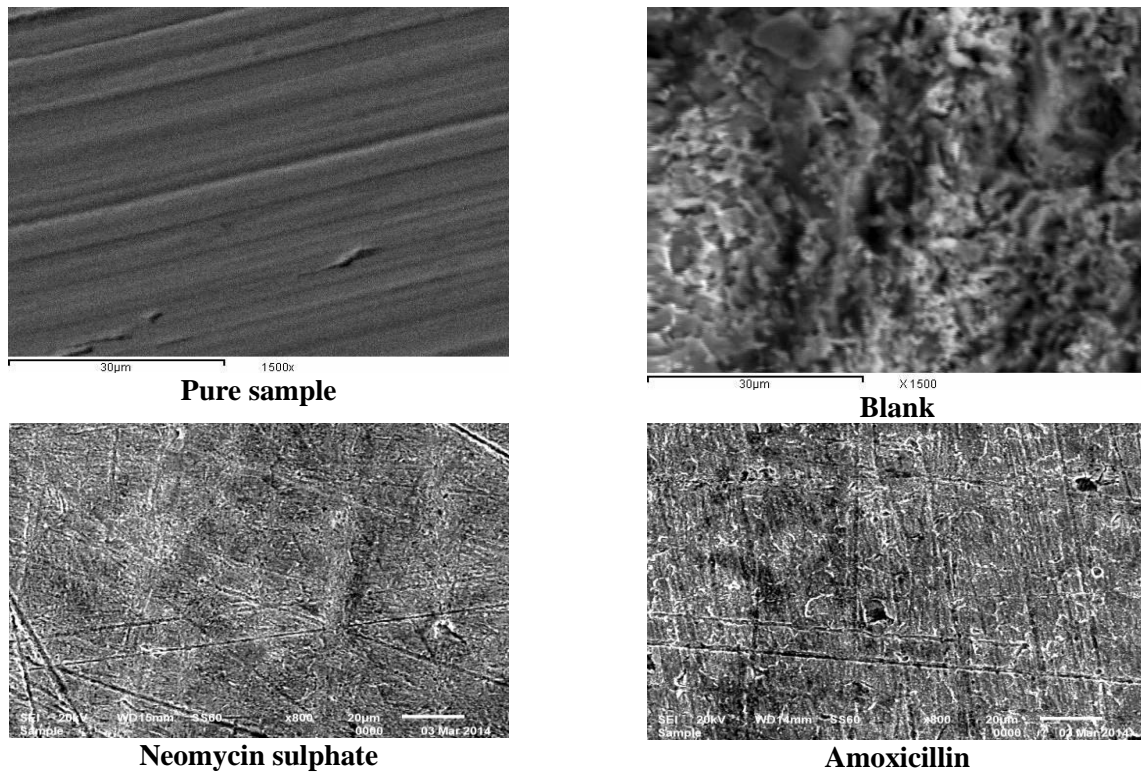
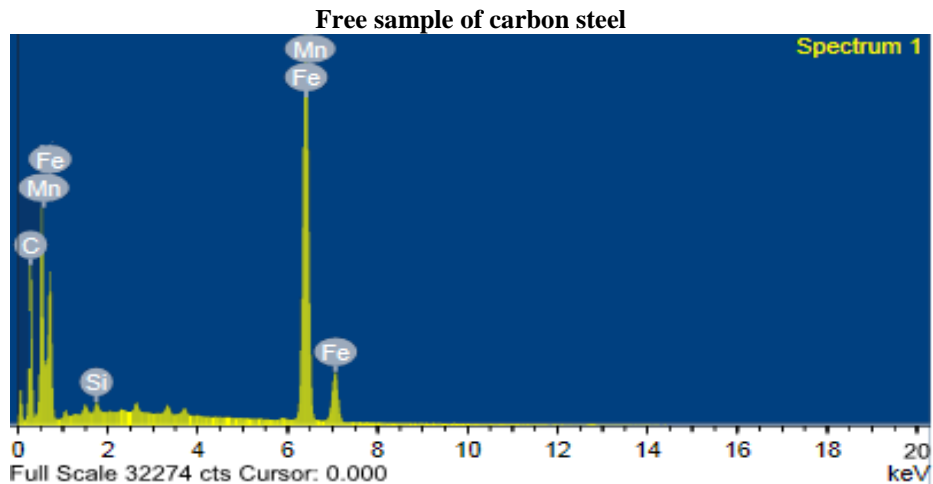


Figure (11): SEM micrographs for carbon steel in absence and presence of 15 x10⁻⁶ M of investigated compounds.



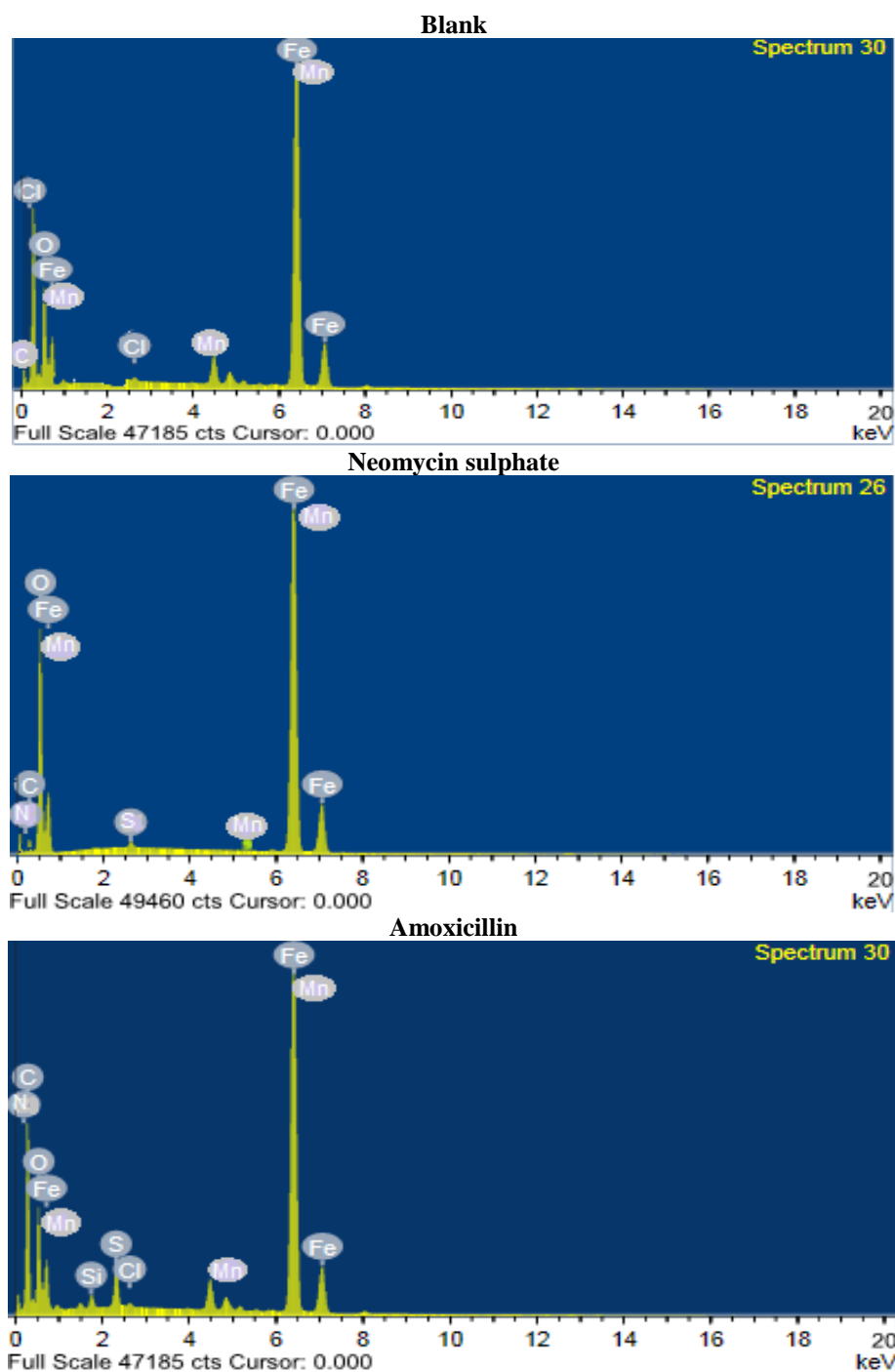


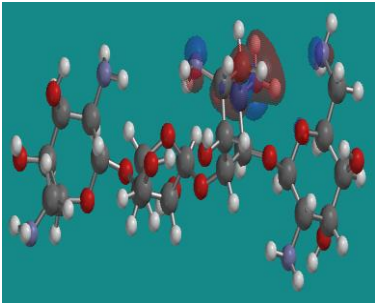
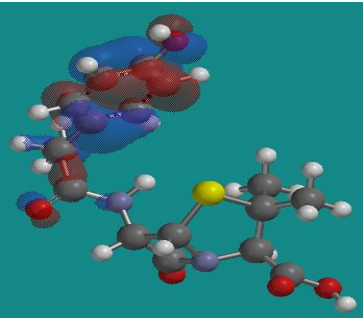
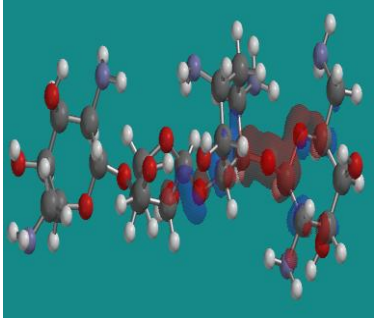
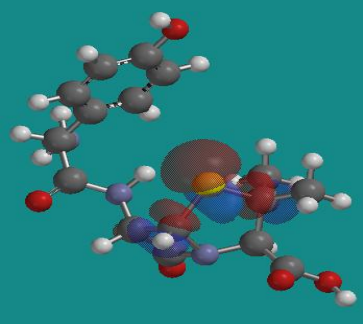
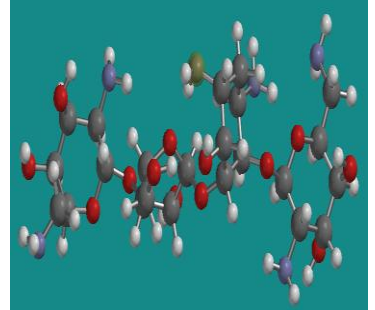
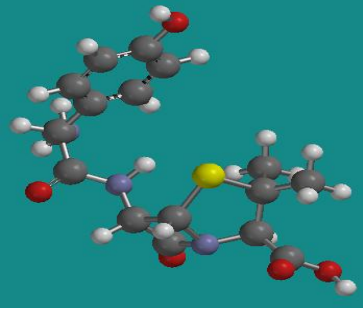
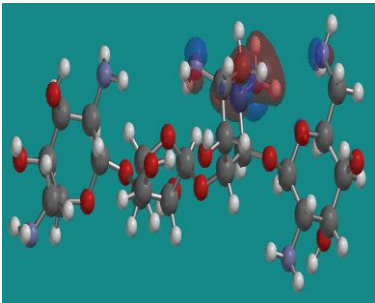
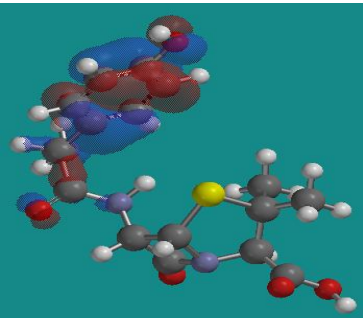
Figure (12): EDX analysis on C-steel in presence and absence of antibiotic compounds for 3 days immersion.

Table (8): Surface composition (weight %) of C-steel after 3h of immersion in HCl without and with 15×10^{-6} M concentrations of the studied inhibitors.

(Mass %)	Fe	Mn	C	O	N	S	Si	Cl
Carbon steel alone	95.58	0.69	3.54	--	--	--	0.19	
Blank	67.98	0.58	2.97	28.09	--	--	--	0.38
Neomycin sulphate	73.25	0.73	6.89	17.21	1.65	0.27	--	--
Amoxicillin	70.47	0.62	4.70	22.35	1.08	0.48	0.09	0.21

3.2.7. Quantum chemical parameters of investigated compounds

The EHOMO indicates the ability of the molecule to donate electrons to an appropriated acceptor with empty molecular orbitals but ELUMO indicates its ability to accept electrons (Figure 13). The lower the value of ELUMO, the more ability of the molecule is to accept electrons [47]. While, the higher is the value of EHOMO of the inhibitor, the easier is its offering electrons to the unoccupied d-orbital of metal surface and the greater is its inhibition efficiency. The calculations listed in Table(9) showed that the highest energy EHOMO is assigned for the compound (A), which is expected to have the highest corrosion inhibition among the investigated compounds. The HOMO–LUMO energy gap, ΔE approach, which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems. The smaller is the value of ΔE , the more is the probable inhibition efficiency that the compound has [48, 49]. The dipole moment μ , electric field, was used to discuss and rationalize the structure. It was shown from Table (9) that compound (A) molecule has the smallest HOMO–LUMO gap compared with the other molecules. Accordingly, it could be expected that compound (A) molecule has more inclination to adsorb on the metal surface than the other molecules. The higher is the value of μ , the more is the probable inhibition efficiency that the compound has. The calculations showed that the highest value of μ is assigned for the compound (A) which has the highest inhibition efficiency. Absolute hardness and softness σ are important properties to measure the molecular stability and reactivity. A hard molecule has a large energy gap and a soft molecule has a small energy gap. Soft molecules are more reactive than hard ones because they could easily offer electrons to an acceptor. For the simplest transfer of electrons, adsorption could occur at the part of the molecule where σ , which is a local property, has the highest value. In a corrosion system, the inhibitor acts as a Lewis base while the metal acts as a Lewis acid. Bulk metals are soft acids and thus soft base inhibitors are most effective for acidic corrosion of those metals. Accordingly, it is concluded that inhibitor with the highest σ value has the highest inhibition efficiency Table (9) which is in a good agreement with the experimental data. This is also confirmed from the calculated inhibition efficiencies of molecules as a function of the inhibitor chemical potential, P_i , and the fraction of charge transfer, ΔN to the metal surface. The relatively good agreement of P_i and ΔN with the inhibition efficiency could be related to the fact that any factor causing an increase in chemical potential would enhance the electronic releasing power of inhibitor molecule Table (9). Analysis to estimate the adsorption centers of inhibitors has been widely reported and it is mostly used for the calculation of the charge distribution over the whole skeleton of the molecule. There is a general consensus by several authors that the more negatively charged heteroatom is, the more is its ability to adsorb on metal surface through a donor–acceptor type reaction. Variation in the inhibition efficiency of the inhibitors depends on the presence of electro negative O- and N-atoms as substituents in their molecular structure.

	Neomycin sulphate	Amoxicillin
HOMO		
LUMO		
Mulliken charges		
	Neomycin sulphate	Amoxicillin
HOMO		

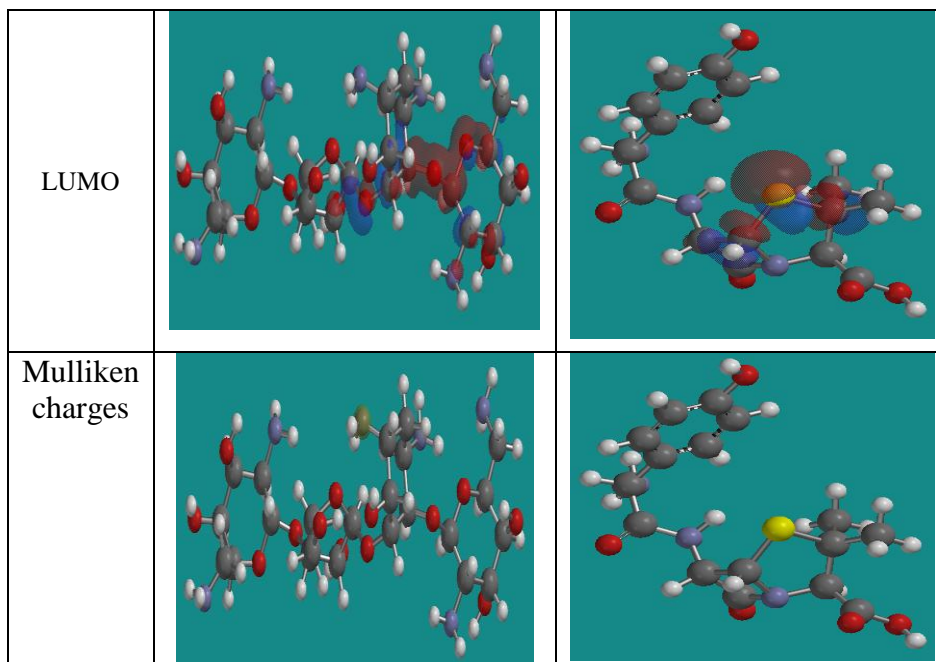


Figure 13: Molecular orbital plots and Mulliken charges of organic compounds.

3.2.8. Electrochemical frequency modulation technique (EFM)

EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current value without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring [50]. The great strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses. Figure (14) shows the frequency spectrum of the current response of pure carbon steel in 1 M HCl, contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies. The EFM intermodulation spectrums of carbon steel in 1 M HCl acid solution containing (15×10^{-6} M) of neomycin sulphate are shown in Figure (15). Similar results were recorded for the other concentrations of the investigated compounds (not shown). The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors (CF-2 and CF-3). These electrochemical parameters were listed in Table (10). The data presented in Table (10) obviously show that, the addition of any one of tested compounds at a given concentration to the acidic solution decreases the corrosion current density, indicating that these compounds inhibit the corrosion of carbon steel in 1 M HCl through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are verified and of good quality [42]. The inhibition efficiencies IE EFM % increase by increasing the studied inhibitor concentrations and was calculated as follows:

$$\% \text{IE}_{\text{EFM}} = [(1 - i_{\text{corr}} / i_{\text{corr}}^{\circ})] \times 100 \quad (13)$$

Where i_{corr}° and i_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively. The inhibition sufficiency obtained from this method is in the order: neomycin sulphate > amoxicillin.

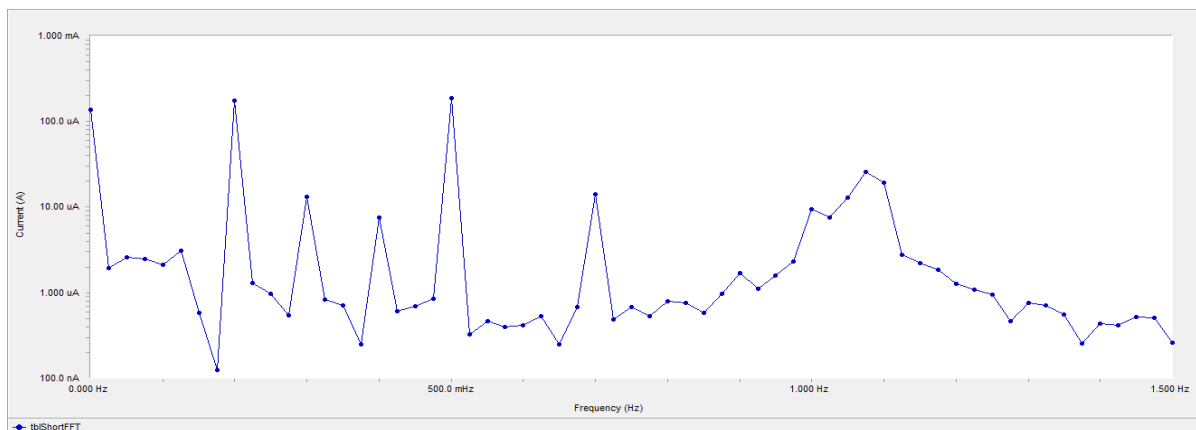


Figure (14): EFM spectra for C-steel in 1 M HCl (blank) at 30° C.

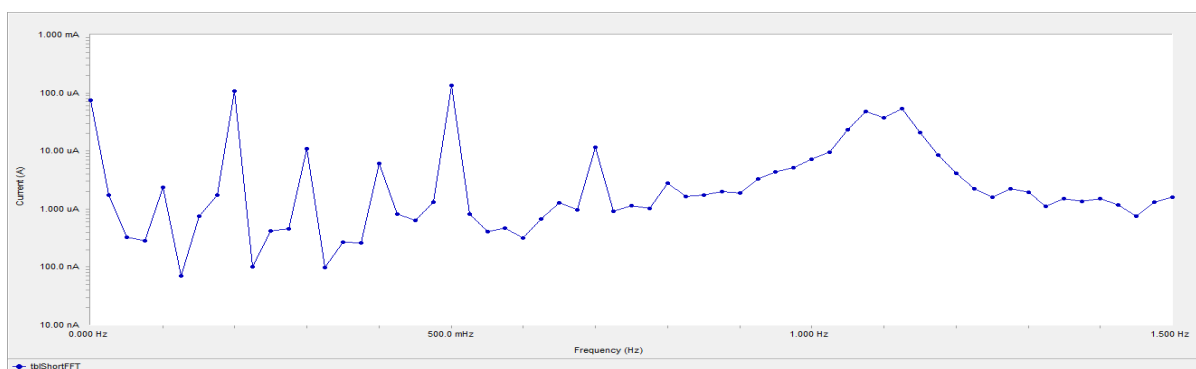


Figure (15): EFM spectra for carbon steel in 1 M HCl in the presence of 15×10^{-6} M from neomycin sulphate at 30° C.

Table (9): The calculated quantum chemical parameters for investigated compounds by using PM3

PM3	(1) Neomycin sulphate	(2)Amoxicillin
E_{HOMO} (eV)	-9.03	-9.14
E_{LUMO} (eV)	-1.66	-1.16
ΔE (eV)= $E_{LUMO} - E_{HOMO}$	7.37	7.98
Dipole moment (Debye)	2.63	2.46
Area (Å^2)	592.58	457.01

Table (10): Electrochemical kinetic parameters obtained by EFM technique for carbon steel in 1 M HCl solutions containing various concentrations of the antibiotic derivatives at 30° C.

Comp.	Conc., M .	$i_{corr.}$, $\mu\text{A cm}^2$	β_a , mV dec^{-1}	β_c , mV dec^{-1}	CF-2	CF-3	% Y_{EFM}
Neomycin sulphate	5x 10 ⁻⁶	170	55.5	69.4	2.01	3.07	59.6
	7 x 10 ⁻⁶	150.4	83.6	107.1	1.67	3.03	64.3
	9 x 10 ⁻⁶	132.3	49.6	60.02	1.9	3.2	68.5
	11 x 10 ⁻⁶	109.4	56.3	86.5	1.97	3.53	74.0
	13 x 10 ⁻⁶	84.3	59.8	70.6	1.89	2.86	79.9
	15x 10 ⁻⁶	66.7	95.2	81.6	1.73	3.24	84.2
Amoxicillin	5x 10 ⁻⁶	208.2	125.2	212.8	1.84	3.80	50.6
	7 x 10 ⁻⁶	185	116	143.9	2.23	2.68	56.1
	9 x 10 ⁻⁶	160.3	89.6	120.9	1.96	2.60	61.9
	11 x 10 ⁻⁶	143.5	76.5	85.04	2.79	1.99	65.9
	13 x 10 ⁻⁶	119	65.8	106	1.67	2.95	71.8
	15x 10 ⁻⁶	90	46.2	50.2	2.29	2.91	78.6

4. Mechanism of corrosion inhibition

The adsorption of antibiotic derivatives can be attributed to the presence of polar unit having atoms of nitrogen and oxygen and aromatic/heterocyclic rings. Therefore, the possible reaction centers are unshared electron pair of hetero-atoms and π -electrons of aromatic ring [50]. The adsorption and inhibition effect of antibiotic derivatives in 1 M HCl solution can be explained as follows: In aqueous acidic solutions, antibiotic derivatives exist either as neutral molecules or as protonated molecules and may adsorb on the metal/acid solution interface by one and/or more of the following ways: (i) electrostatic interaction of protonated molecules with already adsorbed chloride ions, (ii) interaction between unshared electron pairs of hetero-atoms and vacant d-orbital of iron surface atoms. In general, two modes of adsorption are considered on the metal surface in acid media. In the first mode, the neutral molecules may be adsorbed on the surface of carbon steel through the chemisorption mechanism, involving the displacement of water molecules from the carbon steel surface and the sharing electrons between the hetero- atoms and iron. The inhibitor molecules can also adsorb on the carbon steel surface on the basis of interaction between unshared electron pairs of hetero-atoms and vacant d-orbital of iron surface atoms. In the second mode, since it is well known that the steel surface bears positive charge in acid solution, so it is difficult for the protonated molecules to approach the positively charged carbon steel surface due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, thus they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, the protonated antibiotic derivatives adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus there is a synergism between adsorbed Cl^- ions and protonated phenolic derivatives. Thus we can conclude that inhibition of carbon steel corrosion in 1 M HCl is mainly due to electrostatic interaction. The decrease in inhibition efficiency with rise in temperature supports electrostatic interaction. Neomycin sulphate has the highest percentage inhibition efficiency. This is due to: its higher molecular size, presence of large number of heteroatoms which may serve as adsorption centers and the presence of larger numbers of benzene rings than amoxicillin.

5. Conclusions

The investigated antibiotic derivatives inhibit the corrosion of carbon steel in 1 M HCl. The inhibition is due to adsorption of the inhibitor molecules on the carbon steel surface by blocking its active sites. Adsorption of antibiotic derivatives fits Freundlich isotherm. Results obtained from weight loss, DC polarization, and AC impedance techniques are reasonably in good agreement and show increased inhibitor efficiency with increasing inhibitor concentration. Polarization data showed that the used inhibitors act as mixed-type inhibitor in 1 M HCl.

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