Cefadroxil Drug as Corrosion Inhibitor for Aluminum in 1 M HCl Medium: Experimental and Theoretical Studies

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Abstract: *the inhibition performance of Cefadroxil drug on Aluminum (Al) in 1 M hydrochloric acid solution was investigated in the temperature range of 298-318k and the concentration range of 0.02-2mm by weight loss and Tafel polarization method. The results show that Cefadroxil can inhibit the corrosive action of hydrochloric acid media. The maximum inhibition efficiency of 93.22% and 90.30% were observed in the presence of 2mM inhibitor in the case of weight loss and potentiodynamic polarization respectively. The adsorption of the studied inhibitor on the Aluminum was found to follow Langmuir adsorption model. Thermodynamic adsorption functions ($\Delta G^0_{ads}, \Delta H^0_{ads}, \Delta S^0_{ads}$) and the activation parameters ($E_a, \Delta H^*_a, \Delta S^*_a$) were determined and analyzed. The results withdrawn from these parameters indicated spontaneous adsorption of the inhibitor on the metal surface and a strong interaction with the metallic surface. Tafel polarization showed that Cefadroxil behaves as mixed-type inhibitor. Surface analysis using Scanning Electron Microscopy (SEM) has confirmed the existence of a protective film of inhibitor molecules onto Al surface. Moreover, Density Functional Theory (DFT) calculations with 6-31G (d, p) basis set were carried out in order to elucidate adsorption and reactive sites of the inhibitor. The local reactivity has been analyzed through Mulliken population analysis. The obtained theoretical results are consistent with the experimental data.*

Key Words: *Corrosion inhibition, Aluminum, Hydrochloric acid, Cefadroxil, Weight loss, Adsorption, Potentiodynamic polarization, Quantum chemical.*

I. Introduction

Aluminum [1, 2] is one of the most used metals for several engineering and industrial applications including automotive, aerospace, containers, radiators, electronic devices and building industry due to its cost effectiveness and excellent properties. Because of these excellent and useful properties, Aluminum and its alloys are deployed in various environments containing acids, alkalis and salt solutions where they undergo corrosive attacks despite the existence of a protective oxide film on their surface for corrosion resistance [3]. Hydrochloric acid solutions are normally used for pickling of aluminum and electrochemical etching processes that normally lead to substantial loss of metal due to corrosion [4]. Among numerous ways to protect aluminum from acid corrosion, the most effective and practical method [5, 6] to slow down corrosion processes is the addition of organic corrosion inhibitors to the metal's environment. It is reported [7, 8] that the adsorption of these compounds is influenced by the electronic structure of inhibiting molecules, the steric factor, aromaticity, electron density at the donor site, the functional group and also the polarisability of the group. Previous studies revealed that heterocyclic compounds [9] are employed as corrosion inhibitors because of the presence of various adsorption centers (O, N, S, P, and π electrons) which can help to form complexes with metal ions. Unfortunately, the Use of some organic chemical inhibitors is limited by diverse reasons especially their costly synthesis, poor biodegradability, toxic and hazardous for human beings and the environment as well. For this purpose, the natural products of plant origin or drugs are a better choice due to the fact that they are environmentally benign and contain incredibly rich source of naturally synthesized organic compounds among which most of them are known to have inhibitive action. Plant extracts are often insoluble in aqueous media and extraction efficiencies are mainly low. The choice of some drugs used as corrosion inhibitors is based on the following justifications: (a) drugs are mainly soluble in aqueous media, (b) drug molecules contain oxygen, nitrogen and sulphur as active centers, (c) drugs are reportedly environmentally friendly and important in biological reactions and (d) drugs can be easily produced and purified [10-13].

The Aim of the present paper is to highlight the relationship between the calculated quantum chemical parameters and the experimentally determined inhibition efficiency of Cefadroxil drug (**Scheme 1**) against aluminum corrosion in 1M HCl. This can be achieved by computing the most relevant electronic properties of the studied compound including E_{HOMO}, E_{LUMO}, energy Gap (ΔE), dipole moment (μ), electronegativty (χ), global hardness (η), fraction of electrons transferred (ΔN) and charges (δ) on atoms.

Scheme 1: Chemical structure of Cefadroxil.

II. Experimental

II.1 Aluminum Specimen
The samples of aluminum used in this study were in the form of rods with 10 mm as length and 2.5 mm as diameter which is the type AA 1060 and purity of 99.6%.

II.2 Reagents
Cefadroxil (7β - {[(2r) -2-amino-2- (4-hydroxyphenyl) acetyl] amino} -2, 3-didehydrocepham-2-carboxylic acid) of analytical standard with $C_{16}H_{17}N_3O_5S$ as formula was purchased from Sigma-Aldrich Chemicals and used as inhibitor. It is a first-generation cephalosporin antibiotic drug that is the para-hydroxy derivative of cefalexin, and is used similarly in the treatment of mild to moderate susceptible infections such as the bacterium *streptococcus pyogenes*, causing the disease popularly called strep throat or streptococcal tonsillitis, urinary tract infection, reproductive tract infection, and skin infections. Analytical grade 37% hydrochloric acid solution from Sigma-Aldrich Chemicals was used to prepare the corrosive aqueous solution. Acetone of purity 99.5% was also purchased from Sigma-Aldrich Chemicals.

II.3 Solution-Preparation
The solution was prepared by dilution of the commercial hydrochloric acid solution using double distilled water. The blank was a 1 M HCl solution. Solutions of 1M HCl containing Cefadroxil with concentrations in the range of 0.02–2mm were prepared.

II.4 Weight Loss Method
Prior to all measurements, the aluminum samples were mechanically abraded with different grade emery papers (1/0, 2/0, 3/0, 4/0, 5/0, and 6/0). The specimens were washed thoroughly with double distilled water, degreased and rinsed with acetone and dried in a moisture-free desiccator. Weight loss measurements were carried out in a beaker of 100 mL capacity containing 50 mL of the test solution. The immersion time for weight loss was 1h at a given temperature. In order to get good reproducible data, parallel triplicate experiments were performed accurately and the average weight loss was used to calculate the corrosion rate (w), the degree of surface coverage (Θ) and the inhibition efficiency (IE) using Equation 1-3 respectively:

$$W = \frac{m_1 - m_2}{St} \tag{1}$$

$$\theta = \frac{W_0 - W}{W_0} \tag{2}$$

$$IE(\%) = \left(\frac{W_0 - W}{W_0}\right) * 100 \tag{3}$$

where W_0 and W are the corrosion rate without and with inhibitor respectively, m_1 and m_2 are the weight before and after immersion in the corrosive aqueous solution respectively, S is the total surface of the aluminum specimen and t is the immersion time.

II.5 Tafel Polarization Method
Each test was carried out at room temperature (298K). Measurements were conducted with an Autolab PGSTAT 20 Potentiostat (Ecochemie, Utrecht Netherlands) driven by GPES 4.4 Software. The electrochemical behavior of al sample in the inhibited and uninhibited solution was studied by recording anodic and cathodic

potentiodynamic polarization curves. Prior to each measurement, the working electrode was immersed in the test solution for 30 min, to establish a steady state open circuit potential Eocp. Measurements were performed in 1M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from $-1500mV/SCE$ to $+500mV/SCE$ versus corrosion potential at a scan rate of 1mV/s. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (j_{corr}). The inhibition efficiency (IE %) was calculated using Equation 4:

$$IE(\%) = \left(\frac{j_{corr}^0 - j_{corr}^{inh}}{j_{corr}^0}\right) \times 100 \tag{4}$$

where j_{corr}^0 and j_{corr}^{inh} are referred to the corrosion current density without and with the addition of the inhibitor, respectively.

II.6 Surface Characterization
The Scanning Electron Microscopy (FEG SEM, SUPRA 40VP, ZEISS, Germany) was used to study the morphology of the aluminum surface after its treatment in the presence or absence of Cefadroxil for 1 h immersion at room temperature. Comparison was made between the bare sample and the immersed ones.

II.7 Computational Details
The present quantum chemistry calculations have been performed with Gaussian 09 series of program package [14]. In our calculations, we have used Becke's three parameter exchange functional along with the Lee–Yang–Parr non local correlation functional (B3LYP) [15] using 6-31G (d, p) basis Set.

Figure 1: Optimized structure of Cefadroxil by B3LYP/6-31G (d, p)

The molecular descriptors such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), the dipole moment ($\mu$) and the total energy (E) of the molecule were computed. The reactivity parameters were then calculated using the conceptual framework of DFT [16, 17]. So, the chemical potential μ_p is defined as (Equation 5):

$$\mu_p = \left(\frac{\partial E}{\partial N}\right)_{v(r)} = -\chi \tag{5}$$

Where μ_p is the chemical potential, E is the total energy, N is the number of electrons, v(r) is the external potential of the system and χ is the global electronegativity. The global hardness is given by Equation 6:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \tag{6}$$

Using the finite difference approximation and the Koopmans theorem, the global electronegativity and the global hardness are given by Equation 7-8 respectively:

$$\chi = \frac{(I+A)}{2} \approx -\frac{(E_{HOMO} + E_{LUMO})}{2} \tag{7}$$

$$\eta = \frac{(I-A)}{2} \approx \frac{(E_{LUMO} - E_{HOMO})}{2} \tag{8}$$

The global softness which is the reciprocal of the global hardness can be obtained using Equation 9:

$$S = \frac{1}{\eta} \tag{9}$$

The ionization potential is the negative of E_{HOMO} (Equation 10)

$$I = -E_{HOMO} \tag{10}$$

The electron affinity is the negative of E_{LUMO} (Equation 11)

$$A = -E_{LUMO} \tag{11}$$

The electrophilicity index ω [18] is defined as:

$$\omega = \frac{\mu_p^2}{2\eta}$$ (12)

According to the definition, this index measures the propensity of chemical species to accept electrons. A high value of electrophilicity index describes a good electrophile behavior while a small value of electrophilicity index describes a good nucleophile behavior.

The fraction of electrons transferred (ΔN) is given by Equation 13 [19]:

$$\Delta N = \frac{\Phi_{Al} - \chi_{inh}}{2(\eta_{Al} + \eta_{inh})}$$ (13)

The values of experimental work function $\Phi_{Al} = 4.28\ eV$ [20] and hardness $\eta_{Al} = 0$ [21] (since for bulk metallic atoms $I = A$) were considered to calculate ΔN. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment [22].

III. Results And Discussions

III.1 Weight Loss Measurements

III.1.1 Effect of inhibitor concentration and temperature on corrosion rate

In order to study the Cefadroxil effect on Al corrosion, weight loss of Al was investigated in 1M HCl. The variation of corrosion rate and inhibition efficiency versus temperature for different concentrations of cefadroxil is displayed in **Figure 2A&B**.
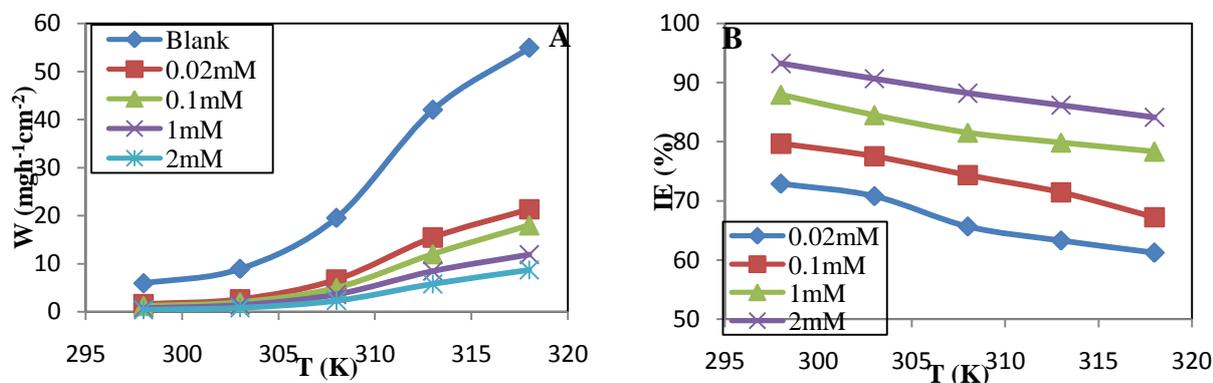
Figure 2: A) Evolution of corrosion rate And B) Inhibition efficiency versus temperature for different concentrations of Cefadroxil.

From **Figure 2A**, it is obvious that the corrosion rates in 1 M HCl solution with the addition of Cefadroxil decreases as the concentration of the studied drug increases. These results highlight the fact that the adsorption of inhibitor on the aluminum increases with increase in inhibitor concentration. The inhibition efficiency reaches a value of 93.22% for the concentration of 2 mM at 298K (**Figure 2B**). the inhibitive action of the inhibitor may be due mainly to the presence of heteroatoms such as oxygen, nitrogen, sulfur and aromatic rings with π-bonds in cefadroxil structure and its ability with this heteroatoms to create a protective film on the metal corroding surface [23]. As shown in **Figure 2B**, inhibition efficiency decreases when the temperature rises. this occurs due to the desorption effect of the inhibitor molecules [24]. Moreover, decrease in inhibition efficiency with increase in temperature is assigned to physical adsorption mechanism and may be explained by increase in the solubility of the protective films and of any reaction products precipitated on the surface [25, 26] of Al metal that may otherwise inhibit the corrosion process.

III.1.2 Adsorption isotherms and thermodynamic functions

Given that adsorption isotherms study provides useful knowledge about the interaction of inhibitors on the metal surface, attempts were made to fit Θ values to various isotherms including Flory-Huggins, Temkin, Freundlich and Langmuir. By fitting the degree of surface coverage (Θ) and the inhibitor concentration (**Figure 3A**), the mean value of the linear correlation coefficients (r^2) obtained graphically is 0.9987 (very close to unity). This result suggests that Langmuir is the suitable adsorption isotherm. According to this isotherm Θ is related to inhibitor concentration C_{inh} by (Equation 14) [27]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$ (14)

Where K_{ads} is the equilibrium constant of the adsorption process.
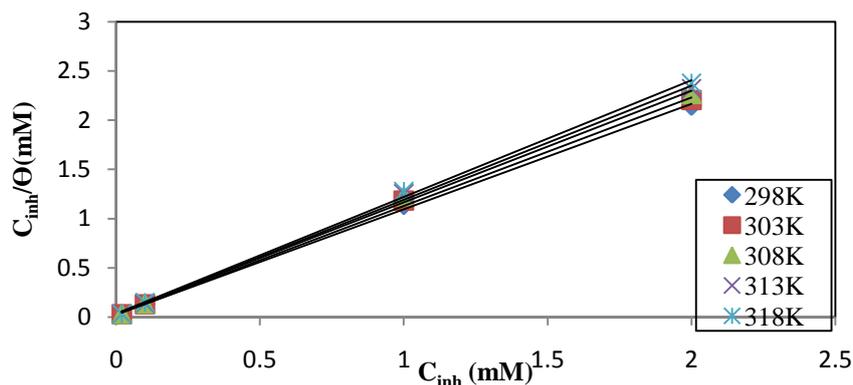
Figure 3A: *Langmuir adsorption isotherm for Cefadroxil on aluminum surface in 1M HCl.*
The obtained Langmuir adsorption parameters for different temperatures are displayed in **Table 1.**

Table1: Regression Parameters of Langmuir isotherm.

Isotherm Model	T(K)	R^2	Slope	Intercept
Langmuir	298	0.9991	1.0716	0.0229
	303	0.9987	1.1030	0.0263
	308	0.9984	1.1338	0.0304
	313	0.9985	1.1593	0.0318
	318	0.9987	1.1856	0.0341

As presented in **Table 1**, it can be clearly seen that the slopes are also very close to unity. This result indicates that Langmuir is the suitable adsorption model. The equilibrium constant (K_{ads}) was related to the standard free adsorption enthalpy by the following Equation [28]:

$$\Delta G_{ads}^0 = -RTln(55.5K_{ads}) \tag{15}$$

In the above equation [29], 55.5 is the concentration of water in mol. L^{-1}, T is the absolute temperature while R is the perfect gas constant. The values of, ΔG_{ads}^0 and the other thermodynamic functions are summarized in **Table 2**.

Table 2: Adsorption thermodynamic functions.

T(K)	K_{ads}(M^{-1})	ΔG_{ads}^0 (kJ mol^{-1})	ΔH_{ads}^0 (kJ mol^{-1})	ΔS_{ads}^0 (J mol^{-1}K^{-1})
298	43668.12	−36.40		
303	38022.81	−36.67		
308	32894.74	−36.90	−15.408	70.20
313	31446.54	−37.38		
318	29325.51	−37.80		

The negative values of ΔG_{ads}^0 indicate that the adsorption process is spontaneous and the adsorbed layer on the aluminum surface is stable [8]. Generally [30-32], values of −20 kJmol^{-1} or less negative are consistent with the electrostatic interactions between the charged metal and the inhibitor i.e. physisorption. The Values Around −40 kJmol^{-1} or more negative are associated with chemisorption, as a result of sharing or transfer of unshared electron pair or π-electrons of organic molecules to the metal surface to form a coordinate type of bond. In our work, free adsorption enthalpy change ranges from −37.80 to −36.40 kJmol^{-1} indicating both physisorption and chemisorption. The standard adsorption enthalpy change ΔH_{ads}^0 and the standard adsorption entropy change ΔS_{ads}^0 are correlated with standard Gibbs free energy through the relation:

$$\Delta G_{ads}^0 = \Delta H_{ads}^0 - T\Delta S_{ads}^0 \tag{16}$$

ΔH_{ads}^0 and ΔS_{ads}^0 are obtained respectively as the intercept and the negative of the slope of the straight line obtained by plotting ΔG_{ads}^0 versus T (**Figure 3B**). The change in adsorption enthalpy ΔH_{ads}^0 is negative, showing an exothermic process. The literature [33] stated that an exothermic process means either physisorption or chemisorption. Therefore this result confirms that the process of adsorption is both physisorption and chemisorption. The change in standard adsorption entropy ΔS_{ads}^0 is positive, meaning that disorder increases during the adsorption process. This situation can be explained by desorption of water molecules replaced by the inhibitor.
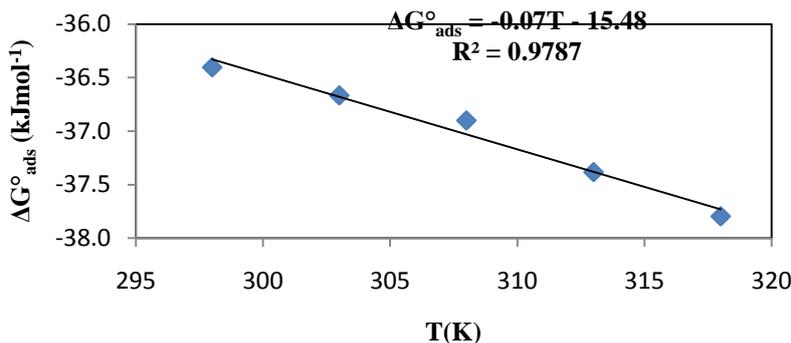
Figure 3B: Free Adsorption Enthalpy ΔG_{ads}^0 versus Temperature (T)

III.1.3 Effect of the temperature and activation parameters

Temperature is an important parameter in metal dissolution studies [34]. Activation parameters are also of great importance in the study of the inhibition processes. the kinetics functions for the dissolution of aluminum without and with various concentrations of the tested compound are obtained [35] by applying the Arrhenius equation and the transition state equation:

$$logW = logA - \frac{E_a}{2.303RT} \tag{17}$$

$$log\left(\frac{W}{T}\right) = [log(\frac{R}{\aleph h}) + \frac{\Delta S_a^*}{2.303R}] - \frac{\Delta H_a^*}{2.303RT} \tag{18}$$

In These Equations, E_a Is The Apparent Activation Energy, A Is The Arrhenius Pre-Exponential Factor; h Is The Planck's Constant, $\aleph$ Is The Avogadro Number, ΔS_a^* Is The Change In Activation Entropy And ΔH_a^* Is The Change In Activation Enthalpy.

Figure 3C and **Figure 3D** show respectively the plots $logW$ and $log\left(\frac{W}{T}\right)$ versus $\frac{1}{T}$
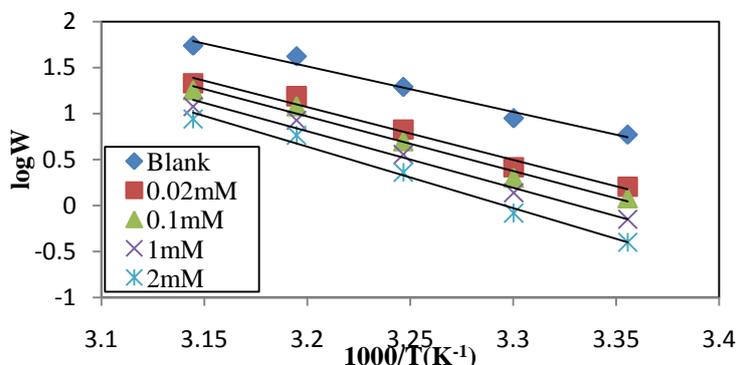
Figure 3C: Arrhenius plots for different concentrations of Cefadroxil in 1M HCl

All graphs show, both in absence and presence of the studied inhibitor excellent linearity as expected from equations (17) and (18), respectively. The intercepts of the lines in **Figure 3C** allow the calculation of the values of the pre-exponential factor (A) and the slopes ($-\frac{E_a}{2.303R}$) lead to the determination of the activation energy E_a both in the absence and presence of the inhibitor.
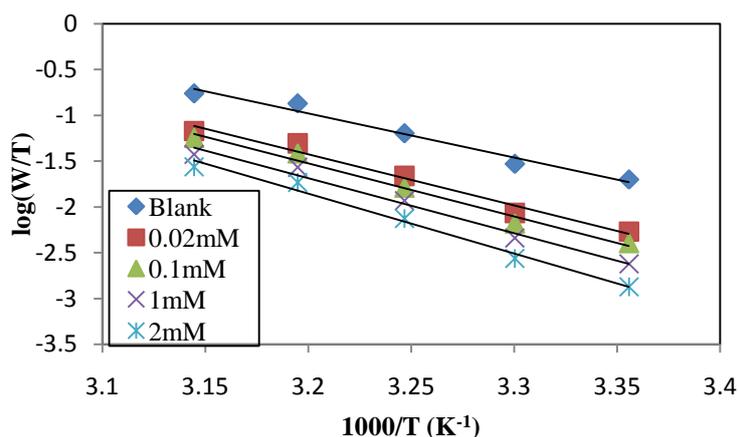
Figure 3D: *Transition state plots of the adsorption behavior of Cefadroxil.*

The straight lines obtained by plotting $log\left(\frac{W}{T}\right)$ versus $\frac{1}{T}$ have $\left(-\frac{\Delta H_a^*}{2.303\,R}\right)$ as slope and $\left[log\left(\frac{R}{\aleph h}\right)+\frac{\Delta S_a^*}{2.303\,R}\right]$ as intercept. Consequently, the values of ΔH_a^* and ΔS_a^* were calculated and presented in **Table 3**.

Table 3: Calculated activation energy, activation enthalpy change and activation entropy change.

System	E_a(kJmol^{-1})	ΔH_a^*(kJmol^{-1})	ΔS_a^*(Jmol^{-1}K^{-1})
Blank	94.77	92.09	78.73
0.02mM	109.69	107.00	117.93
0.1mM	113.58	110.88	128.45
1mM	117.54	114.83	138.00
2mM	127.85	125.12	167.74

From **Table 3**, it seems that E_a and ΔH_a^* varied in the same manner increasing with the concentration, probably due to the thermodynamic relation between them ($\Delta H_a^* = E_a - RT$). The literature [36] states that physical adsorption is associated with, E_a values of the inhibited solution larger than that of the free acid solution (blank). In our work, the uninhibited solution is associated with E_a value, less than that of the inhibited solutions, confirming the predominance of physisorption. since corrosion primarily occurs at surface sites free of adsorbed inhibitor, the higher E_a values in inhibited solutions imply that the inhibitor mechanically screens the active sites of al surface thereby decreasing the surface area available for corrosion [4]. The change in activation enthalpy ΔH_a^* has a positive sign, denoting an endothermic activation process. The shift towards positive value of entropy (δ*s*) imply that the activated complex in the rate determining step represents dissociation rather than association, meaning that disordering increases on going from reactants to the activated complex [37].

III.2 Tafel polarization
For the purpose of detecting the anodic, cathodic or mixed nature of the studied inhibitor, potentiodynamic polarization measurements have been carried out. potentiodynamic polarization curves for Al metal in 1 M HCl solution with different concentrations of Cefadroxil drug are displayed in **Figure 4**. Electrochemical parameters associated with Tafel polarization measurements such as anodic and cathodic tafel slopes (b_a and b_c), corrosion potential (E_{corr}) and corrosion current density (j_{corr}) are calculated and given in **Table 4**. It can be observed from **Figure 4** that in the presence of inhibitors both the anodic and cathodic curves are shifting towards lower current density. Also as inhibitors are added, j_{corr} values are going to decrease (**Table 4**), which reveals that inhibitor molecules are adsorbed on the metal surface.
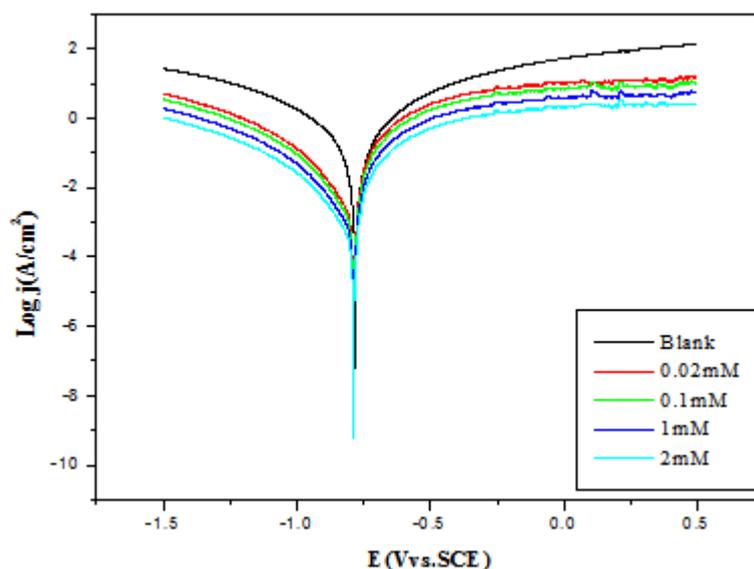
Figure 4: *Tafel polarization curves for aluminum in 1 M HCl without and with different concentrations of Cefadroxil*

Table 4: Potentiodynamic polarization parameters for the corrosion of Al in 1M HCl solutions without or with various concentrations of Cefadroxil.

C_{inh}(mM)	E_{corr}(mVvs.SCE)	j_{corr}(μA/cm^2)	b_a(mV/dec)	$-b_c$(mV/dec)	IE(%)
0 (Blank)	−783.53	201.06	154.85	115.32	-
0 .02	−828.39	60.20	143.19	124.26	70.06
0 .1	−825.18	47.36	142.52	125.60	76.44
1	−820.91	32.06	146.04	122.23	84.05
2	−814.50	20.04	147.66	109.93	90.03

As presented in **Table 4**, it was found that the slopes of the cathodic and anodic tafel lines are almost constant and independent on the inhibitor concentration meaning that the inhibiting action of the tested compound occurred by simple blocking of the available surface area. In the other hand, the inhibitor decreased the surface area available for anodic dissolution and hydrogen evolution without affecting the reaction mechanism [38]. In addition, the values of (E_{corr}) do not shift beyond ±85mV in the presence of inhibitor, suggesting that cefadroxil acts as a mixed-type inhibitor [39, 40]. Moreover, the Tafel polarization data are consistent with the earlier weight loss results obtained.

III.3 Surface Characterization
Scanning electron micrographs of Al surface before and after immersion in 1M HCl without and with inhibitor are shown in **Figure 5 A-C**.
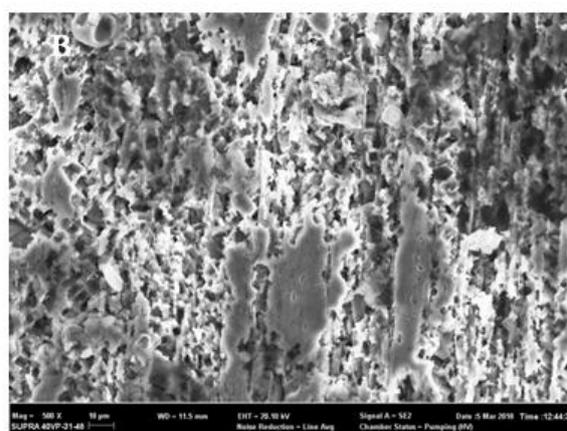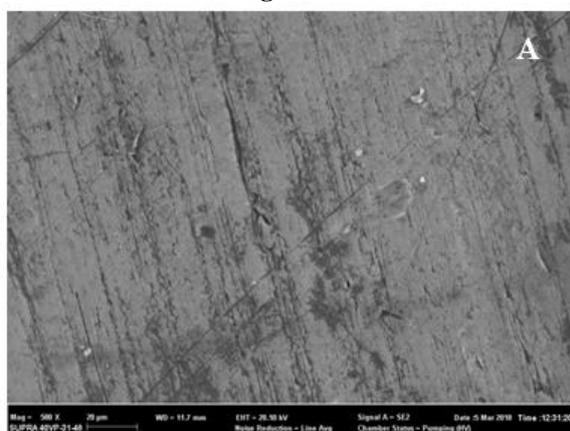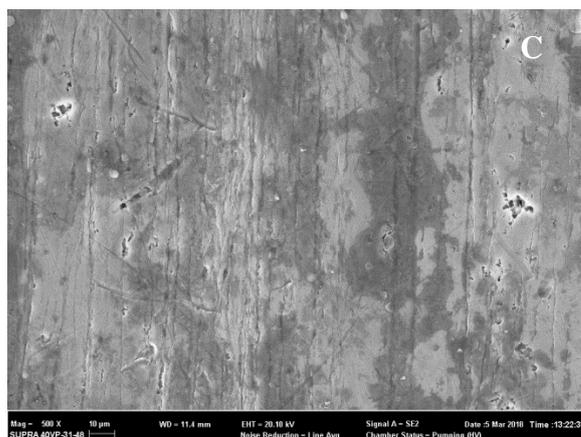
Figure 5: SEM images of aluminum (A) Before 1h of immersion in 1M Hcl, (B) After 1h of immersion in 1 M HCl solution without inhibitor and (C) After 1h of immersion in 1 M HCl solution with optimum concentration of Cefadroxil (2mM).

As presented in **Figure 5 A**, the metallic sample before immersion in 1M HCl seems smooth and shows fewer pits and cracks. **Figure 5 B**) shows aggressive attack of the corroding medium on the aluminum surface. The corrosion products appear too uneven, arranged layer upon layer and the metallic surface presents high roughness because of pits and cracks. From **Figure 5 C**, it is obvious that the Aluminum surface seems to be almost unaffected by corrosion due to the adsorption of Cefadroxil which was forming a thin inhibitor film of the drug onto aluminum surface. These results prove that Cefadroxil drug protects effectively the metal surface by covering it with a protective layer which separates Al from the corrosive environment, confirming the earlier gravimetric and electrochemical results.

III.4 Quantum chemistry study
The calculated quantum chemical parameters are displayed in **Table 5**.

Table 5: Quantum chemical parameters of Cefadroxil.

Descriptor	Value	Descriptor	Value
E_{HOMO} (eV)	−6.0965	I (eV)	6.0965
E_{LUMO} (eV)	−1.4525	A (eV)	1.4525
ΔE (eV)	4.6440	μ (Debye)	4.5054
ΔN	0.1089	Ɲ (eV)	2.3220
S (eV)$^{-1}$	0.4306	ω	2.0780
χ (eV)	3.7745	TE (a.u)	−1558.5177

The frontier molecular orbital (FMO) theory reveals that the reactive ability of an inhibitor is closely related to the HOMO and LUMO energies. Higher value of E_{HOMO} for a given molecule [41] indicates its electron-donating ability to an appropriate acceptor with low empty energy orbital. In our case the HOMO Energy (E_{HOMO}= −6.0965 eV) which can be considered as a high value when compared with values reported [42] could explain the high inhibition efficiency of the studied molecule. The LUMO energy orbital is consistent with electron accepting ability of a molecule. Lower value of E_{LUMO} for a molecule [38] implies good electron accepting ability. The obtained value (E_{LUMO}= −1.4525 eV) is low when compared with that of some molecules in the literature [43]; so, the studied molecule could receive electrons from the aluminum metal. The energy gap, ($\Delta E = E_{LUMO} − E_{HOMO}$) is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As ΔE decreases, the reactivity of the molecule increases leading to increase in the inhibition efficiency of the molecule. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low [26]. In our case, the low value of energy gap ($\Delta E = 4.6440$ eV) could explain the high inhibition efficiency values (IE= 93.22% and 90.30% for C_{inh}=2 mM at T = 298 K respectively by weight loss and Tafel polarization measurements). HOMO and LUMO diagrams of the inhibitor are given in **Figure 6A&B**.
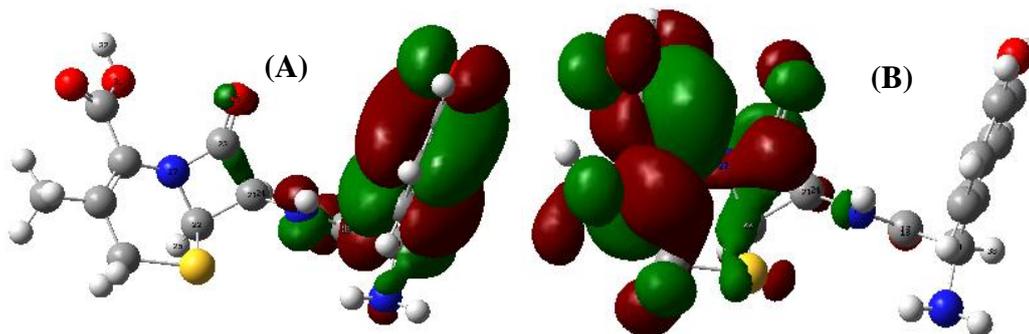
Figure 6: *HOMO (A) and LUMO (B) of Cefadroxil by B3LYP/6-31G (d, p)*

From **Figure 6A&B**, it can be seen that the HOMO is in the region containing the phenyl ring and four heteroatoms while the LUMO is in the region containing the antibiotic function and six heteroatoms. So, these regions are probably the active areas where transfers of electrons could be done (from the molecule to Aluminum or vice-versa).

Ionization energy *I* and electron affinity *A* are two important parameters associated with the HOMO and LUMO energies. The ionization potential (*I*) and the electronic affinity (*A*) are respectively (6.0965 eV) and (1.4525 eV). This low value of (*I*) and the high value of electron affinity indicate the capacity of the molecule both to donate and accept electron. The dipole moment (μ in Debye) is another important electronic parameter that results from non uniform distribution of charges on the various atoms in the molecule. The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [44]. The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Aluminum surface. The volume of the inhibitor molecules also increases with the increase of μ. This increases the contact area between the molecule and surface of aluminum and increasing the corrosion inhibition ability of Cefadroxil. In Our work the value 4.5054 (Debye) of the studied inhibitor shows its better inhibition efficiency.

Electronegativity (χ), hardness (η) and softness (*S*) are very useful parameters in chemical reactivity theory. electronegativity indicates the capacity of a system to attract electrons, whereas hardness and softness express the degree of reactivity of the system. In our study, the electronegativity of the studied molecule (χ_{inh} =3.7745 eV) is lower than the metal's work function (ϕ_{Al} =4.28 eV), showing that aluminum has the better attraction capacity. This situation leads to a positive value of electron transferred (ΔN = 0.1089) indicating a possible motion of electrons from the inhibitor to the metal. the electrophilicity index (ω) [18] measures the propensity of chemical species to accept electrons; a high value of electrophilicity index describes a good electrophile while a small value of electrophilicity describes a good nucleophile. In our case the high value (ω = 3.0678 eV) expresses the electrophile character of the studied molecule showing the possible transfer of electrons from the metal to the inhibitor. The literature [45-47] pointed out that the use of Mulliken population analyses to probe adsorption centers of inhibitors have been widely reported. **Figure 6C** shows the Mulliken charge densities calculated on the optimized geometry of Cefadroxil using the B3LYP/6-31G (d, p) method.
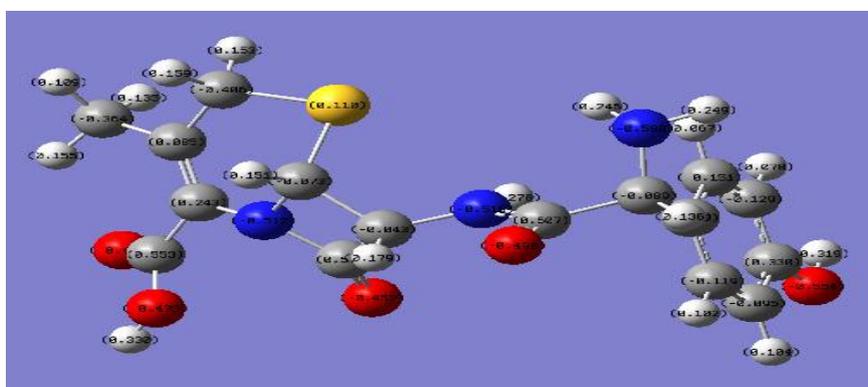
Figure 6C: *Mulliken charges on the optimized structure of Cefadroxil using B3LYP/6-31G (d, p).*
Several authors [48-50] state that the more negatively charged an heteroatom is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction. It has also been reported that electrophiles attack

molecules at sites of negative charges [49], which means that sites of ionic reactivity can be estimated from atomic charges in a molecule. Thus the values of Mulliken charges of selected atoms of Cefadroxil are listed in **Table 8**. It is possible to observe that the possible sites for adsorption and reactivity of the studied molecule are 11O, 14N, 18O, 19N, 26O, 27N, 30O and 31O.

Table 8: Mulliken charges (with hydrogen summed into heavy atoms) for selected atoms of the compound.

Atom	11O	14N	18O	19N	26O	27N	30O	31O
Charge	-0.554	-0.588	-0.498	-0.518	-0.452	-0.512	-0.477	-0.473

As displayed in **Table 8** and **Figure 6C**, one can see that all the heteroatoms excepted sulfur have high charge densities. Therefore, they are active centers (adsorption centers), which could have strongest ability to bond the metal surface [49].

III.5 Mechanism of Inhibition

The inhibition efficiency of Cefadroxil (CFL) against the corrosion of al in 1 M HCl can be explained on the basis of the adsorption sites, their charge density, molecular size, molecular structure, which contains heteroatoms such as nitrogen, oxygen and sulfur with lone pair electrons. However, in an acid medium, the studied compound could be protonated since it contains heteroatoms. Thus, it becomes cation, existing in equilibrium with the corresponding molecular form as follow:

$$CFL + XH^+ \leftrightarrow [CFLH_x]^{X+} \tag{19}$$

Due to their specific adsorption and their small degree of hydratation, chloride ions (Cl^-) from hcl firstly adsorbed on the positively charged [51] metal surface (Al^{3+} ions cover the surface of the metal) and create an excess negative charge along the metal surface towards the solution side, what leads to the adsorption of the protonated form of the inhibitor. Therefore, a protective layer due to the electrostatic interaction between the charged species from the inhibitor and the chloride ions is formed (physisorption). The positive sign of fraction of electron transferred shows that electrons can be transferred from the inhibitor species to the aluminum. The electronic configuration of al is $1S^2 2S^2 2P^6 3S^2 3P^1$. The incompletely filled 3P orbital of Al could bond with HOMO of Cefadroxil while the filled 3S orbital of it could interact with LUMO of Cefadroxil what could explain the existence of chemisorption. So, a probable schematic mechanism (**Figure 7**) can be proposed where the black arrows indicate chemisorption, while the broken lines show the electrostatic interaction between the chloride ions and the cationic form of the inhibitor.
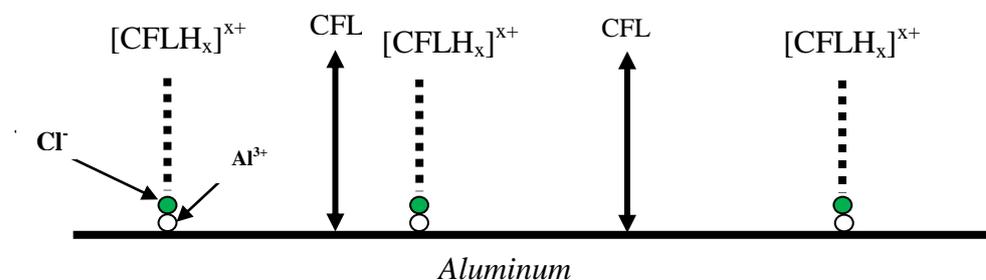
Figure 7: Schematic mechanism of Al corrosion inhibition in 1 M HCl by Cefadroxil

IV. Conclusion

From the results of the study, the inhibition efficiency increases with increasing concentration of the studied compound suggesting that Cefadroxil drug is a good inhibitor for the corrosion of aluminum in one molar hydrochloric acid solution. Adsorption of the studied inhibitor obeys Langmuir adsorption isotherm. The adsorption and activation thermodynamic functions highlight a spontaneous adsorption process of the studied molecule onto aluminum and both physisorption and chemisorption mechanisms with predominance of physisorption. Potentiodynamic polarization reveals that Cefadroxil behaves as a mixed-type inhibitor. Surface characterization by SEM confirms the formation of a protective film covering the surface of the working electrode (Al). Quantum chemical calculations data from B3LYP/6-31G (d, p) are in good agreement with experimental results.

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