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Experimental and computational study of levofloxacin as corrosion inhibitor for carbon steel in acidic media

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ABSTRACT

The corrosion inhibition behaviour of levofloxacin was investigated on carbon steel by means of a 2 M HCl solution, using potentiodynamic polarization measurement and Quantum chemical studies. The inhibitive effect of the studied compound was found to increase with increasing concentration and to increase with increasing temperature. The study reveals that levofloxacin is a mixed-type corrosion inhibitor. The adsorption of levofloxacin on carbon steel surface obeys the Langmuir adsorption isotherm and involves physical adsorption mechanisms. Quantum chemical studies corroborate experimental results.

***Keywords*:** Corrosion Inhibition, Polarization, levofloxacin and Adsorption

1. INTRODUCTION

Corrosion is a naturally occurring phenomenon commonly define as the deterioration of material by chemical interaction with their environment. Corrosion of metals has cause huge economic losses involving billions of dollars each year in many industries. The international measure of prevention, application and economic of corrosion technology (IMPACT) estimated the global cost of corrosion to be $2.5 trillion which is equivalent to 3.4% of Gross Domestic Product GDP (Gerhard, 2001). The IMPACT found that the introduction of corrosion prevention could result in global saving between 15-35% of the cost damage. Therefore control measures or procedures need to be implemented in order to reduce or inhibit corrosion thereby prolonging the life span of metals. Several approaches have been suggested and implemented to protect metal against corrosion. One of the approach is the used of corrosion inhibitor which is one of the best method of controlling corrosion. Most of the corrosion inhibitors used are toxic, expensive and difficult to come by. Thus researchers have focused on the used eco-friendly compounds, that could be obtained conveniently and contain electronegative atoms such as Nitrogen, Sulphure and Oxygen in the relatively long carbon chain compounds.

Presently a few non toxic organic compound such as Azithromycin, Abdullatef (2015); Amoxicillin (Siaka *et al*., 2013); Cefixime, (Naqvi, *et al.*, 2011); Ciprofloxacin (Akpan and Offiong, 2014a); Amoldipine (Akpan and Offiong, 2014b) have been reported as corrosion inhibitor, Nonetheles, there still need for research on other organic compounds to be used as inhibitors in industrial application. The objectives of this study is to investigate the inhibitory action of Levofloxacin as corrosion inhibitor for carbon steel in 2 M HCl solution using Potentiodynamic Polarization and Computational methods (Rokosz, 2016).

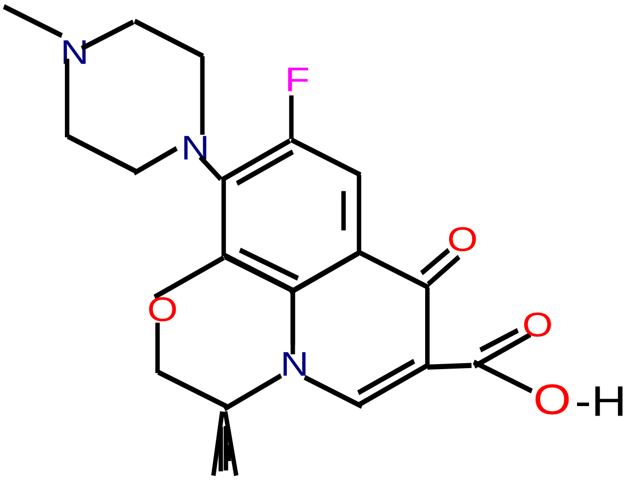
2. EXPERIMENTAL DETAILS

2. 1. Inhibitor

Levofloxacin is an antibiotic drug under the class of fluoroquinolones. It however has order medicinal value.

The IUPAC nomenclature of the drug is 9-fluoro-2,3-dihydro-3-methyl-10-(4-methyl piperazin-1-yl)-7-oxo-7H-Pyrido(12,3-di)-1,4-benzoxazine-6-carboxyclic acid.

With molecular formula $C_{18}H_{20}FN_3O_4$ and molecular weight of 361.368 g/mol. It has the chemical structure as shown in the Figure below.



Levofloxacin

Scheme 1. Chemical Structure of Levofloxacin drug

The Tablet of Levofloxacin was obtained from peace Land Pharmaceutical shop Ndidem Usang Iso Road, Calabar-Nigeria, sold under the trade name "Levaquin" Different concentration of the drug were prepared by dissolving appropriate quantities of the Tablet from the mass of the drug sample (Akpan and Offiong, 2014).

2. 2. Corrosion medium

The corrosive solution of 2 M HCl was prepared from reagent grade of HCl by dilution using doubly distilled water. The concentration of the solution ranges from 50 ppm to 500 ppm.

2. 3. Carbon Steel Specimen

Carbon Steel with 98% of Fe was used for the investigation and this was obtained from cylindrical pipeline which was mechanically press cut into square coupons of about 1 cm × 1 cm and used in the electrochemical experiment as working electrode. The coupons were used after polishing with emery papers. There were degreased in acetone wash with distilled water and finally dried.

2. 4. Electrochemical Experiment

Potentiodynamic Polarization experiment was carried out using a conventional three electrode electrochemical cell assembly. Freshly polished carbon steel specimen with an exposed surface area of 1 cm^2 was used as a working electrode and Saturated calomel electrode (SCE) as reference electrode. The measurements were perform using Gamry Electrochemical Analyzer at 303 K and 323 K potentio- dynamic current- potential curves were recorded by changing the electrode potential E_{corr} automatically with scan rate of 0.5 mVs^{-1} from a low potential -0.25 to + 0.6. Before each run the working electrode was immersed in the test solution for 30 minutes to obtain a steady state. The corrosion rate of the metal was calculated through corrosion current density I_{corr}. The linear Tafel segment of anodic and cathodic curves obtained were extrapolated. The inhibition efficiency IE % was evaluated from the measured I_{corr} values (Ameh *et a.*, 2016; Kumar *et al.*, 2016; Bhawsar *et al.*, 2015).

$$IE\% = \frac{IoCorr - Icorr}{IoCorr} \times 100 \qquad 1$$

where: I_{ocorr} = Blank and I_{corr} = Blank + inhibitor.

2. 5. Computational Details

Quantum Chemical Calculation details

Quantum chemical calculations were carried out with the aid of Gaussian 03 software suit. The structure of levofloxacin was used as the representative structure for computational studies. The initial structures were refined with self consistent field theory (SCF). The Optimized structures obtained from SCF calculations were later optimized by Density Functional Theory DFT which involve the Backe's three Parameter hybride functional and Lee-Yang-Paar Correlation functional (B3LYP). Quantum chemical parameters which include the energy of highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy Gab ($\Delta E = E_{LUMO} - E_{HOMO}$) and dipole moment μ were recorded.

3. RESULTS AND DISCUSSIONS

3. 1. Potentiodynamic Polarization Measurements

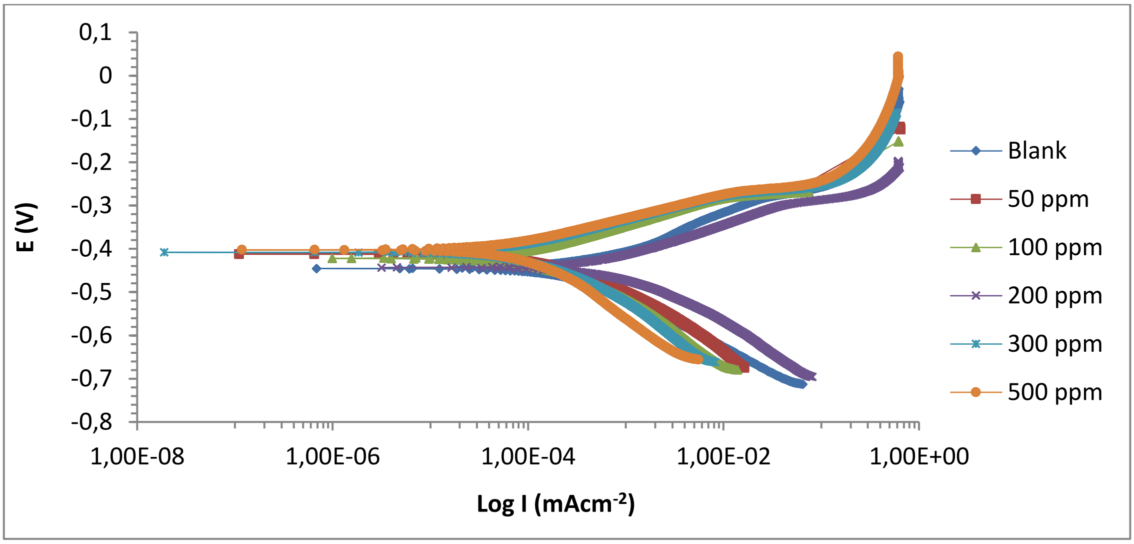


Figure 1. Potentiodynamic Polarization curve for carbon steel in 2 M HCl in the absence and presence of different concentrations of Levofloxacin at 303 K.

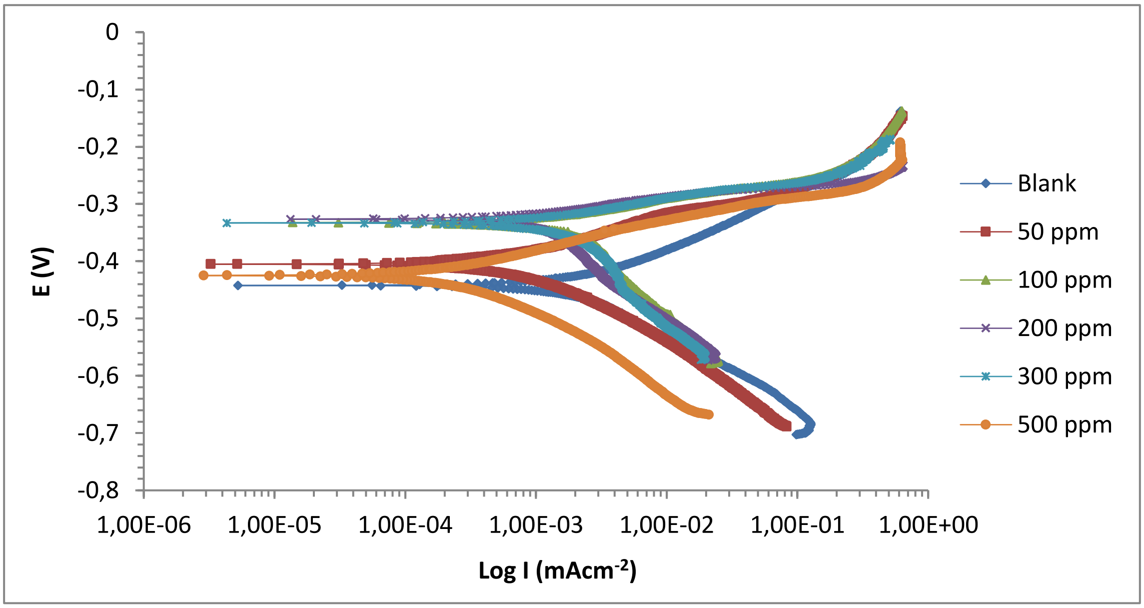


Figure 2. Potentiodynamic Polarization curve for carbon steel in 2 M HCl in the absence and presence of different concentrations of Levofloxacin at 323 K.

Polarization plots for carbon steel in 2 M HCl solution in absence and presence of dissimilar concentrations of (Blank, 50 ppm, 100 ppm, 200 ppm, 300 ppm and 500 ppm) of Levofloxacin are made known in Figure 1 to Figure 2. From the curves it can seen that the cathodic and anodic branches of the Tafel polarization are shifted towards lower current to similar extent in the presence of Levofloxacin, which may be as a result of the blocking effect of the adsorbed inhibitor molecules. It can also be deduced from the plots that the studied inhibitor inhibits corrosion by controlling both cathodic and anodic reactions (mixed type inhibitor). Since the anodic and cathodic reactions are affected by Levofloxacin. This implies that the addition of inhibitor reduces anodic dissolution of carbon steel and also retard the cathodic reaction. Electrochemical parameters deduced from the polarization curve are listed in Table 1. From the results obtained it can be seen that by increasing the concentration of inhibitor, the corrosion current I_{corr} decreased and Inhibition efficiency % IE, polarization resistant increases. Suggesting that inhibitor acted by simply blocking the available surface area (Ameh *et al.*, 2016).

Table 1. Electrochemical Parameters Obtained from Potentiodynamic Polarization curve.

Inhibitors	Conc.	ba $Vdec^{-1}$	bc$Vdec^{-1}$	Ecorr (V)	Icorr (μAcm^{-2})	CR (mpy)	Rp (Ωcm^2)	θ	IE%
	Blank	102	454	-446	560	256	10633		
	50ppm	72	84	-412	98	45	22357	0.8255	82.55
LEVO	100ppm	71	84	-422	92	42	23137	0.8358	83.58
303 K	200ppm	71	79	-417	80	37	24053	0.8573	85.73
	300ppm	64	90	-408	71	32	29029	0.8733	87.33
	500ppm	61	111	-402	65	30	41503	0.8835	88.35
	Blank	116	217	-442	3560	1626	5433		
	50ppm	76	391	-333	3370	1539	9469	0.311	31.10
LEVO	100ppm	61	249	-333	2040	929	5284	0.427	42.28
323K	200ppm	53	541	-326	1770	808	22229	0.503	50.28
	300ppm	74	100	-405	622	284	4752	0.825	82.52
	500ppm	56	87	-425	188	86	8524	0.947	94.71

3. 1. 1. Effect of Temperature

Examination of temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in absence and presence of inhibitor give some insight into the possible means of inhibitor adsorption (Okafor *et al.*, 2010). Increase in inhibition efficiency with increase in temperature with corresponding decrease in corrosion activation energy in the presence of inhibitor compared to its absence is often interpreted as being indicative of formation of chemical adsorption layer, while a decline in inhibition efficiency with ascend in temperature with a corresponding increase in corrosion activation energy in the presence of inhibitor compared to its absence, is attributed to physical adsorption mechanism (Okafor *et al*., 2010; Fouda *et al*., 2016). The trend in inhibition efficiency with temperature obtained are Listed in Table 1. Suggesting Chemical adsorption of the inhibitor on the metal surface. The apparent activation energies E_a, for the dissolution of carbon steel in 2 M HCl in the absence and presence of the inhibitor were calculated from condensed Arrhenius equation.

$$Log\frac{CR2}{CR1} = \frac{Ea}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right) \qquad 2$$

where: CR_1 and CR_2 is the corrosion rate at Temperature T_1 and T_2 respectively. The calculated activation energy values are shown in Table 3. The results indicated that E_a in the presence of the inhibitor is not consistent. This behaviour is an indication of Physical and Chemical adsorption of the studied inhibitor on the metal surface. The evaluation of heat of adsorption Q_{ads} was 0btained from the trend of surface coverage with temperature as follows

$$Qads = 2.303R\left[log\left(\frac{\theta 2}{1-\theta 2}\right) - log\left(\frac{\theta 1}{1-\theta 1}\right)\right] \times \left(\frac{T1\ X\ T2}{T2-T1}\right) \qquad 3$$

where: θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively the estimated values of heat of adsorption are listed in Table 3. The negative values are consistent with inhibitor been a physical adsorption (Fouda *et al*, 2016).

Table 3. Calculated values of activation energy and Heat of adsorption.

Conc.	E_a KJ/mol	Q_{ads} KJ/mol	θ_1	θ_2
Blank	73.33175			
50ppm	140.7051	-57.71	0.8255	0.053
100ppm	122.5659	-78.11	0.8358	0.427
200ppm	123.1439	-72.53	0.8573	0.503
300ppm	86.41877	-15.34	0.8733	0.825
500ppm	43.02858	-35.07	0.8835	0.947

3. 1. 2. Adsorption Isotherm

The possible ways of discussing the mechanism of corrosion inhibition is by adsorption of organic compounds which blocks the metal surface and thus reduced the corrosion process. The adsorption provide the information about the interaction among the adsorbed molecules themselves as well their interaction with the metal surface. Adsorption isotherm are very important to understand the mechanism of heterogeneous organ electrochemical reaction involving solid surfaces. The experimental data were applied to different adsorption isotherm equations. It was found that the experimental data fitted the Langmuir adsorption isotherm as shown in Figure 3 which may be formulated as

$$Log\frac{C}{\theta} = LogC + LogKads \qquad 4$$

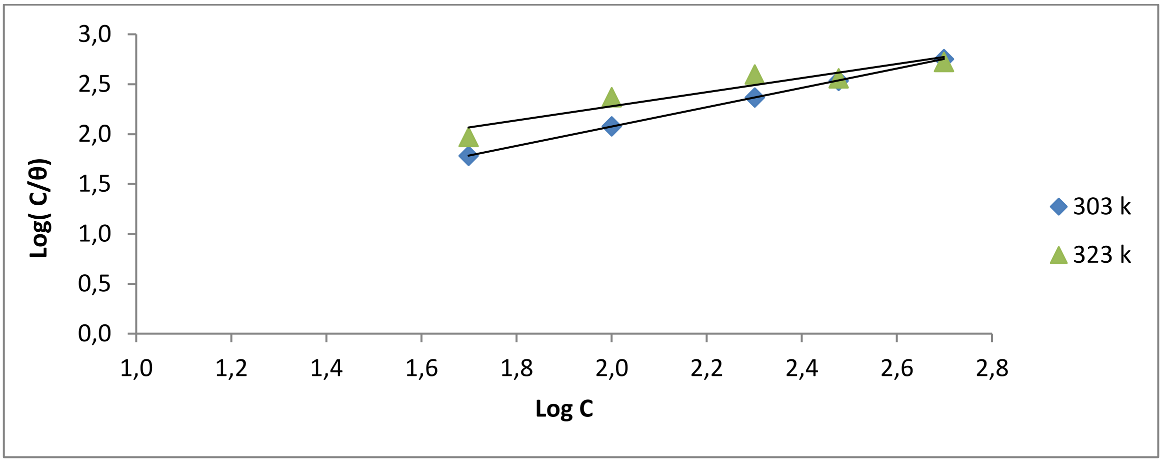


Figure 3. Langmuir adsorption isotherm plot for the adsorption of the Levofloxacin on carbon Steel in 2 M HCl.

This plot are linear with the slope and correlation coefficients (R^2) near unity. The thermodynamic adsorption parameter (ΔGads) was calculated from the equ. 5 at different temperature and listed in Table 4.

$$\Delta G_{ads} = -2.303\ RT \log 55.5\ K_{ads} \qquad 5$$

where 55.5 is the concentration of water in $molL^{-1}$, R is the gas constant, T is the absolute Temperature K_{ads} is equilibrium conatant and ΔG_{ads} is free energy of adsorption.

Table 4. Calculated value of free energy of adsorption.

TEMP. K	K_{ads}	SLOPE	ΔG_{ads}	R2
303	0.138	0.968	-10.92	0.999
323	0.866	0.899	-16.14	0.899

The negative sign of free energy (ΔG_{ads}) in Table 4 indicate that adsorption of the study compounds on the surface of the API 5L X-52 Steel was spontaneous. It is well known from the study of adsorption that values of ΔG_{ads} ranging from -40 $kjmol^{-1}$ and above reflect chemisorptions which involve charge sharing or transfer from the inhibitor molecules to metal surface to form coordinate bond type, whereas those below -40 $kjmol^{-1}$ to 1 $kjmol^{-1}$ signify electrostatic interaction between metal surface and charge organic molecules in the bulk of the solution identify a physisorption. (Fouda *et al*., 2016). Therefore the calculated ΔG_{ads} values are between 10 – 16 $kjmol^{-1}$ indicated that adsorption mechanism of the studied molecules on API 5L X-52 Steel in 2 M HCl solution is physisorption.

3. 2. Quantum Chemical Calculations

Quantum chemical calculations were carried out in order to investigated the adsorption and inhibition mechanism of the studied compound (Bhawsar *et al*., 2015). Fig. 4 shows complete geometric optimization of the studied inhibitor. The HOMO and LUMO (frontier molecular Orbital) present in the Levofloxacin compound are shown in Fig. 5.

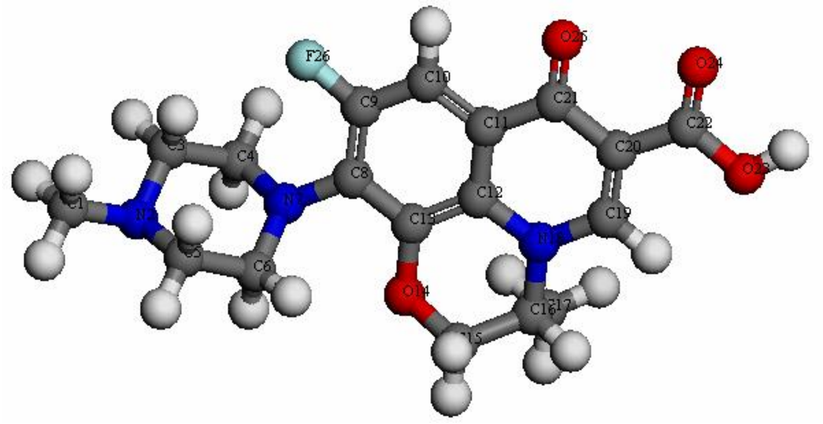
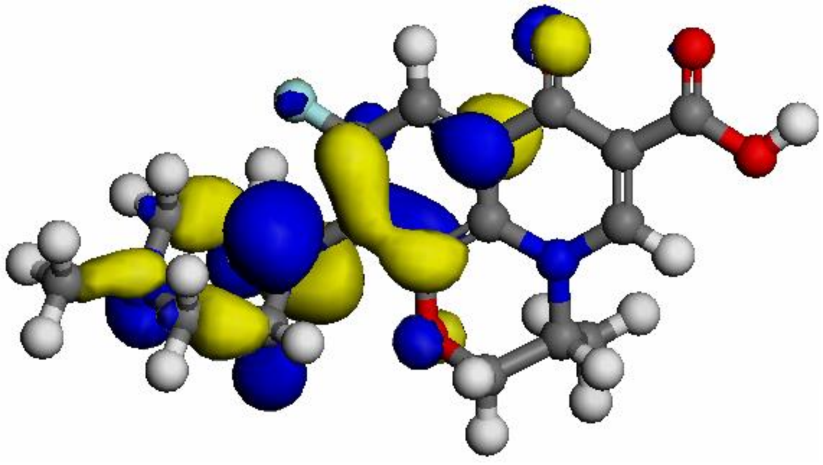
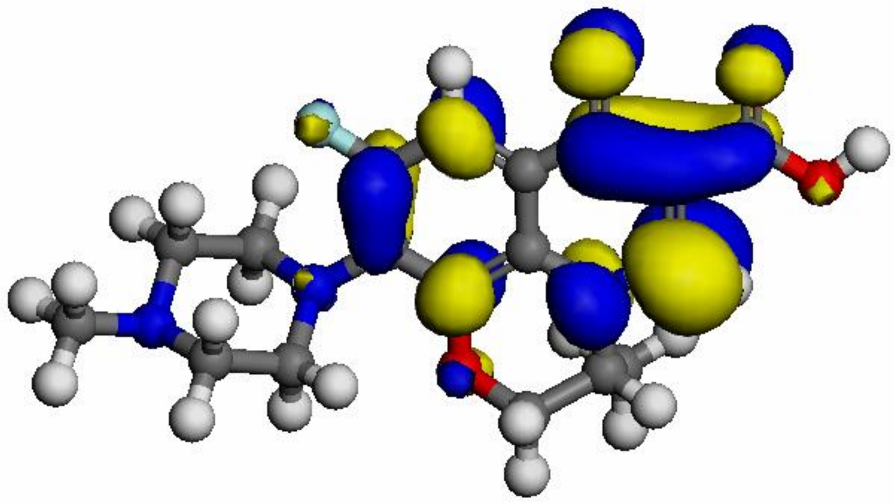


Figure 4. Optimized structure of the studied molecule Levofloxacin.



HOMO



LUMO

Figure 5. Schematic Representation of the HOMO and LUMO of molecular Orbital structure of Levofloxacin.

In order to understand the nature of the interaction of the compound with the metal surface is to focus on the composite index that directly control the electronic interaction of the inhibitor molecules with the metal surface. The index include: E_{HOMO}, E_{LUMO}, ΔE and dipole moment μ. Etc. listed in Table 5 (Bhawsar *et al.*, 2015).

Table 5. Calculated Quantum Parameters for levofloxacin.

E_{HOMO} (ev)	E_{LUMO} (ev)	ΔE (ev)	M (debyes)
-4708	-2.204	2.504	8.955

E_{HOMO} is often connected with the electron donating ability of a molecule, higher energy value of E_{HOMO} revealed the ability of the molecule to donate electron to an empty molecular orbital. Thus increase in E_{HOMO} value facilitate adsorption or inhibition. Therefore the energy of LUMO shows the capability of the molecule to accept electrons, the lower the value of E_{LUMO} the more likely the molecule accept electrons. The lower the value of energy gab (ΔE), the higher the inhibition efficiency because the energy to remove an electron from the last occupied orbaital will be low. And the higher value of dipole moment (μ) favour accumulation of the inhibitor on the surface layer (Bahwsar *et al.*, 2015; Kumar *et al.*, 2016). The adsorption of the inhibitor on the Fe surface takes nearly parallel to the surface so as to maximize it contact with the surface as shown in Figure 6.

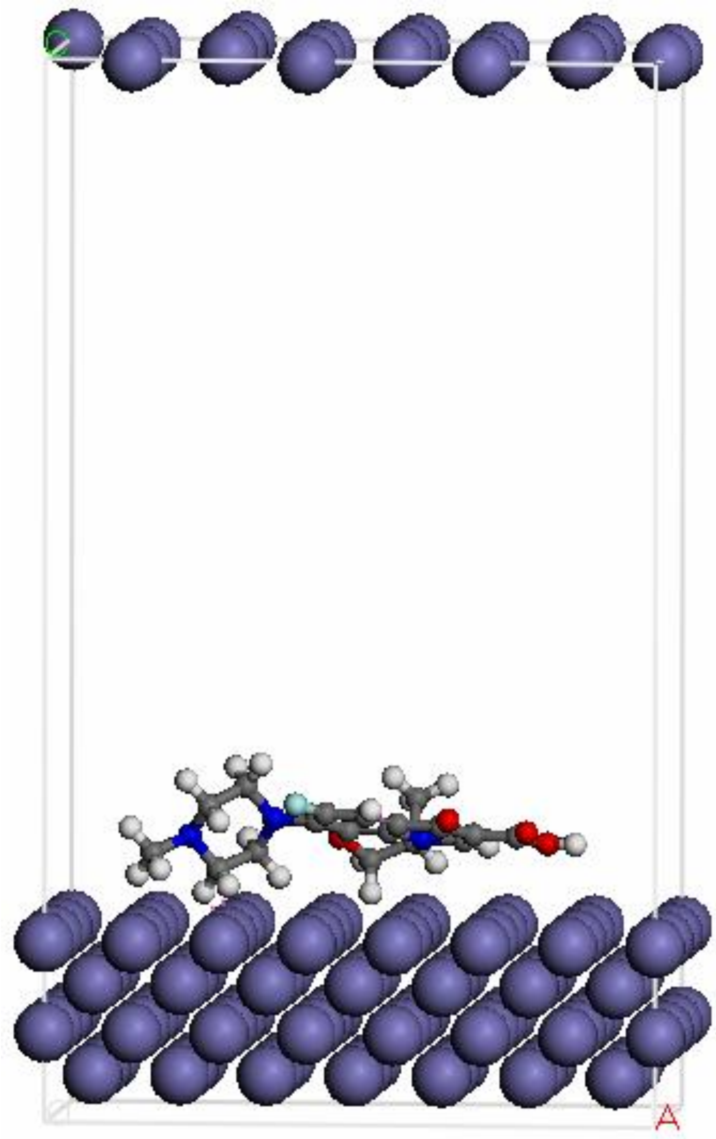


Figure 6. The adsorption of the inhibitor on the Fe surface.

4. CONCLUSIONS

Levofloxacin compound was tested for the corrosion inhibition process on carbon steel in 2 M HCl solution, using Potentiodynamic polarization and Quantum chemical calculations. The following conclusions can be drawn from the study.

1. The inhibition efficiency of the studied compound increases with increasing concentrations
2. The adsorption behaviour of levofloxacin on carbon steel in 2 M HCl obeys Langmuir isotherm and involve physical and chemical adsorption mechanism.
3. Levofloxacin is a good corrosion inhibitor and acted as mixed type.

4. Quantum chemical parameters such as E_{HOMO}, E_{LUMO}, energy gab and dipole moment suggest that levofloxacin has higher corrosion inhibition strength.

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