Ampicillin potentials as Corrosion Inhibitor: fukui function calculations using B3-YLP exchange correlation

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ABSTRACT

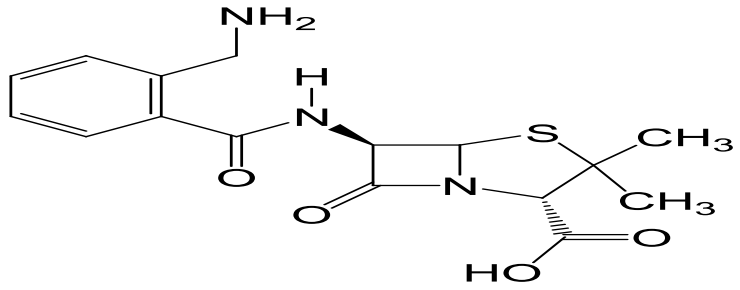
Inhibition and adsorption potentials of ampicillin for the corrosion of mild steel in solutions of HCl have been investigated using empirical and computational approach. The experimental study was carried out using gravimetric and Fourier transform infrared spectroscopy methods of monitoring corrosion while the computational study was carried out using quantum chemical approach via Hyperchem program suit. The results obtained showed that various concentrations of ampicillin inhibited the corrosion of mild steel in solutions of HCl through the mechanism of physiosorption. The adsorption of ampicillin on mild steel surface was found to be exothermic, and spontaneous, and fitted the Langmuir adsorption model. DFT study has been used to identify the site for electrophillic and nucleophillic attack through B3-YLP exchange correlation fukui function computation.

INTRODUCTION

Corrosion is a primary means by which metals deteriorate and is therefore a major industrial problem. The degradation occurs when metals come in contact with moisture, acids, bases, salts, aggressive metal polishes and other liquid chemicals. Other agents of corrosion are gaseous materials like acid vapours, formaldehyde gas, and sulphur containing and ammonia gases. When metals are exposed to corrosion agents within an electrical circuit, they give up electrons to become positively charged ions. Corrosion of mild steel is a major problem in some industries including the oil and fertilizer industries[1]. This is because in these industries, there are some processes (such as scaling, etching, etc) that necessitate contact between mild steel and aggressive medium such as acid, alkaline and salt solutions [2]. In view of the problems created by mild steel corrosion, several researches on the methods of inhibition of its corrosion have been reported and it has been established that the use of inhibitors is one of the best methods of the prevention of the corrosion of mild steel in acidic medium[3, 4].

The choice of inhibitors for the corrosion of metals depends on the ability of

the inhibitor to be synthesised from cheap raw materials and for the inhibitor to be environmentally friendly. Most inhibitors are organic compounds that contain heteroatoms (S, N, O, P) or those that have long carbon chains or aromatic ring systems. Among the compounds investigated and found to be good inhibitors are some drugs[5-16]. Some authors generally agree that drugs are inhibitors that can compete favourably with green corrosion inhibitors and that most drugs can be synthesised from natural products. The choice of some drugs as corrosion inhibitors is based on the following: (a) drug molecules containing oxygen, nitrogen and sulphur as active centres, (b) drugs that are reportedly environmentally friendly and important in biological reactions and (c) drugs that can be easily produced and purified. In this study ampicillin shall be used for the inhibition of the corrosion of mild steel in HCl.



(2S,6R)-6-(2-(aminomethyl)benzamido)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid

Figure 1: Chemical Structure of Ampicillin

MATERIALS AND METHODS

Materials

Materials used for the study were mild steel sheet of composition as determined by quotiometric method, wt%: Mn (0.6), P (0.36), C (0.15), Si (0.03) and 98.86% Fe. The sheet was mechanically pressed cut into different coupons, each of dimension, 5 x 4x 0.11 cm. Each coupon was degreased by washing with ethanol, cleaned with acetone and allowed to dry in the air before preservation in a desiccator. All reagents used for the study were of analar grade and double distilled water was used for their preparation. The concentration of HCl used for weight loss studies was 0.1M.

Methods

Gravimetric Method

In the gravimetric experiment, a previously weighed mild steel coupon was completely immersed in 250 ml of the test solution in an open beaker. The beaker was covered with aluminium foil and inserted into a water bath maintained at 303 K. After every 24 hours, the corrosion product was removed by washing each coupon (withdrawn from the test solution) in a solution containing 50 % NaOH and 100 g/dm^3 of zinc dust. The washed coupon was rinsed in acetone and dried in the air and to constant weight. The experiment was repeated at 333 K. In each case, the difference in weight for a period of 168 hours was taken as the total weight loss. From the average weight loss (mean of three

replicate analyses) results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ) and the corrosion rate of mild steel (CR) were calculated using equations 1, 2 and 3 respectively;

$$\%I = (1 - W_1/W_2) \times 100 \quad 1$$

$$\theta = 1 - W_1/W_2 \quad 2$$

$$CR = \Delta W/At \quad 3$$

where W_1 and W_2 are the weight losses (g) for mild steel in the presence and absence of the inhibitor, θ is the degree of surface coverage of the inhibitor, $\Delta W = W_2 - W_1$, A is the area of the mild steel coupon (in cm^2), t is the period of immersion (in hours) and W is the weight loss of mild steel after time, t.

RESULTS AND DISCUSSION

In Table 1, the inhibition efficiencies ampicillin obtained from gravimetric method are presented. From the results obtained, it is evident that the inhibition efficiencies of the inhibitors increase with increase in concentration of the inhibitors but decrease with increasing temperature. These also suggest that the inhibitors are adsorption inhibitors and that the mechanism of adsorption favours physical adsorption[17].

Fig. 2 shows the plots of weight loss with time in different concentrations of HCl solutions and fig. 3 shows the plot of weight loss with time in different concentrations of ampicillin.

Table 1: Inhibition efficiencies for various concentrations of ampicillin for the corrosion of mild steel in 0.1M HCl

Cg/l	**at 303K**	**at 333K**
0.1	86.51	62.42
0.2	87.75	64.32
0.3	89.01	66.44
0.4	90.05	68.56
0.5	90.25	71.23

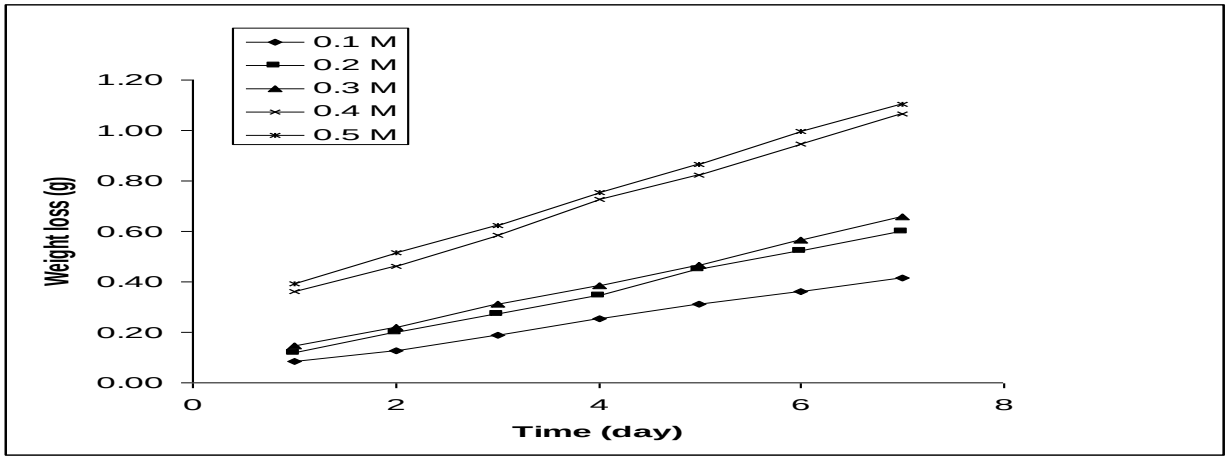


Fig. 2: Variation of weight loss with time for the corrosion of mild steel in various concentrations of HCl.

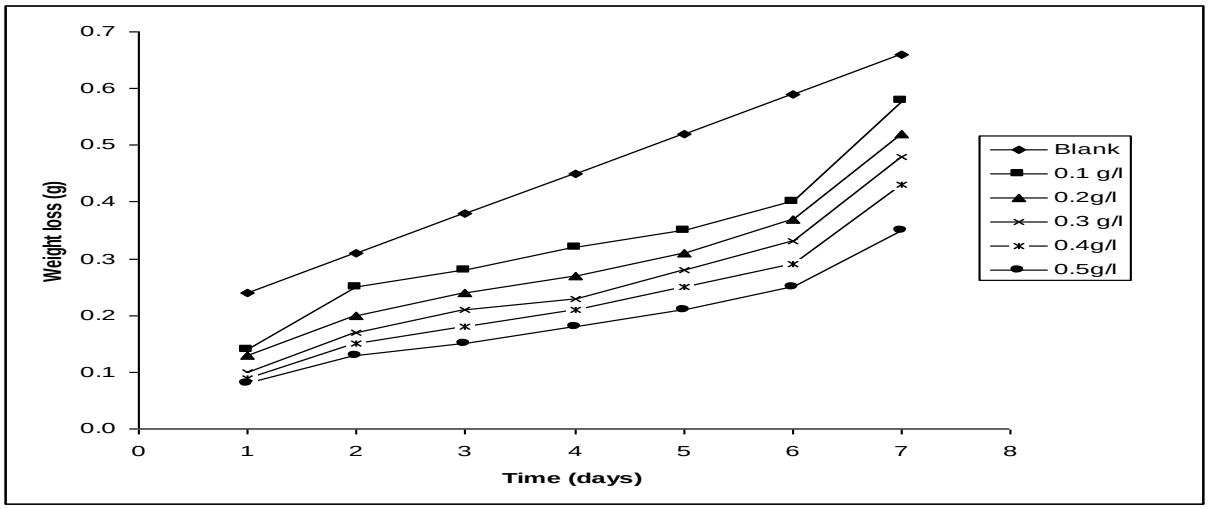


Fig. 3: Variation of weight loss with time for the corrosion of mild steel in 0.1M HCl containing various concentrations of ampicillin

Effect of Temperature

The effect of temperature on the corrosion of mild steel in HCl, in the absence and presence of various concentrations of ampicillin was assessed from the Arrhenius equation which can be represented as equation 4 [18].

$$CR = A\exp(-E_a/RT) \quad 4$$

where CR is the rate of corrosion of mild steel, A is the Arrhenius or pre-exponential constant, E_a is the activation energy, R is the universal gas constant and T is the

temperature. The logarithm of both sides of equation 4 yields equation 5,

$$\log CR = \log A - E_a/2.303RT \qquad 5$$

If the corrosion rates of mild steel at temperatures T_1 (303 K) and T_2 (333 K) are CR_1 and CR_2, then substitutions into equation 5 yields equation 6

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 6$$

The activation energies calculated from equation 6 are presented in Table 2. From the results obtained, it can be seen that the activation energies are below the threshold value of 80kJ/mol expected for the mechanism of chemical adsorption. Therefore, the adsorption of ampicillin on mild steel surface is consistent with the mechanism of charge transfer from the inhibitor's molecule to the charged metal surface, which supports physiosorption mechanism[19].

Table 2: Activation energy and heat of adsorption for the adsorption of ampicillin on mild steel surface

Cg/l	E_a (kJ/mol)	Q_{ads}(kJ/mol)
0.1	31.29	-42.12
0.2	33.45	-44.22
0.3	37.22	-45.23
0.4	38.67	-45.03
0.5	36.12	-46.22

Thermodynamic and Adsorption Considerations

The heat of adsorption of ampicillin on mild steel surface was calculated using equation 7 [20].

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] x\left(\frac{T_{1X}T_2}{T_2 - T_1}\right) kJmol^{-1} \qquad 7$$

where Q_{ads} is the heat of adsorption, R is the universal gas constant, θ_1 and θ_2 are the degrees of surface coverage of the inhibitors at temperatures T_1 and T_2 respectively. From the calculated values of Q_{ads} (Table 2), it can be deduced that the adsorption of the inhibitors on mild steel surface is exothermic. Also, since the reactions were carried out at constant pressure, calculated values of Q_{ads} are expected to be approximately equal to the enthalpy change.

The adsorption characteristics of ampicillin were also studied by fitting data obtained for the degree of surface coverage of the inhibitors into different adsorption isotherms such as Langmuir, Temkin and Freundlich adsorption isotherms etc. The test revealed that the adsorption characteristics of the compounds are best described by the Langmuir adsorption

isotherm, which can be expressed as according to equation 8.

$$\theta = \frac{K_{ads}C}{1+K_{ads}C} \qquad 8$$

where C is the concentration of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage of the inhibitor and K_{ads} is the equilibrium adsorption constant. Transformation of equation 8 yields equation 9,

$$\log(C/\theta) = \log C - \log K_{ads} \qquad 9$$

From equation 9, plots of log(C/θ) versus logC should yield straight lines provided the assumptions establishing the Langmuir adsorption isotherm are valid. Fig. 4 shows the Langmuir isotherms for the adsorption of ampicillin on mild steel surface respectively. The adsorption parameters deduced from the isotherms are presented in Table 3. From the results obtained, it can be seen that the slopes and R^2 values for the Langmuir plots are very close to unity indicating the adsorption data very much fit the Langmuir adsorption model.

The equilibrium adsorption constant of adsorption obtained from the intercept of the Langmuir adsorption isotherms is related to the standard free energy of adsorption according to the equation 10[21].

$$\Delta G^0_{ads} = -2.303RT \log(55.5\ K_{ads}) \qquad 10$$

Calculated vales of the free energy are also presented in Table 3. From the results obtained, the free energies are negatively less than the threshold value of -40kJ/mol required for the mechanism of chemical adsorption. Generally, values of ΔG^0_{ads} between 0 and -20kJ/mol are consistent with the mechanism of charge transfer from charged inhibitor's molecules to charged metal surface. Therefore, the adsorption of ampicillin on mild steel surface is spontaneous with a mechanism of physical adsorption[22].

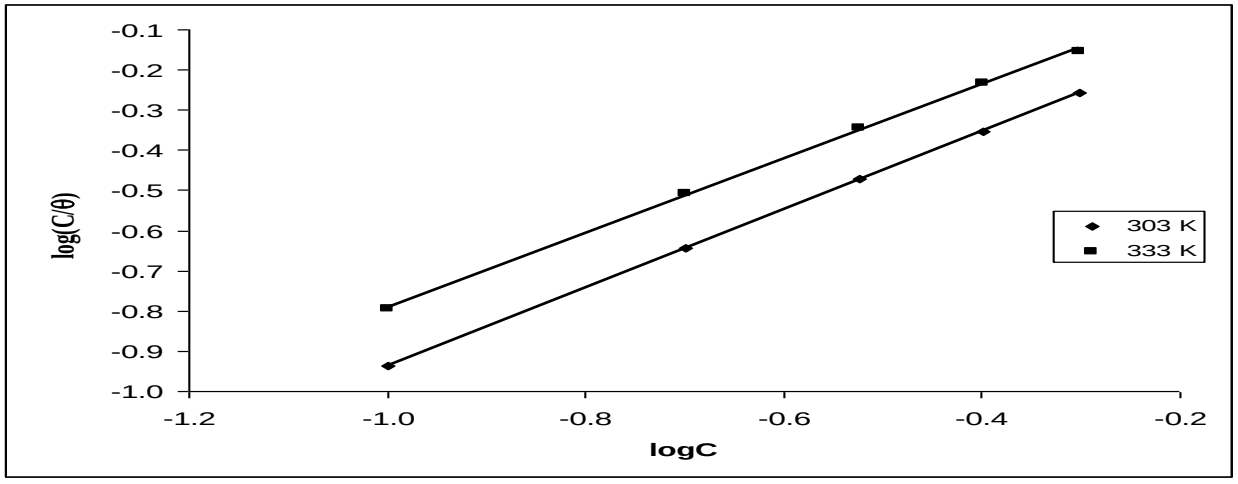


Figure 4: Langmuir isotherms for the adsorption of ampicillin on mild steel surface

Table 3: Langmuir adsorption parameters for the adsorption of ampicillin on mild steel surface

Parameters	**at 303K**	**at 333K**
Slope	0.9721	0.9213
log K_{ads}	0.0358	0.1310
R^2	1.0000	0.9995
ΔG^0 (kJmol^{-1})	-10.30	-10.85

Fourier Transform Infrared (FTIR) Spectra

Figs.5 and 6 show the FTIR spectra of the corrosion of mild steel product in the absence of an inhibitor (blank) and pure sample of ampicillin. Fig. 7 presents the FTIR spectrum of the mild steel corrosion product containing 0.5 g/l of ampicillin. The wavelengths and peaks of IR adsorption by ampicillin are presented in Table 4. The peaks and frequencies of IR adsorption are also presented in Table 4. From the results obtained for ampicillin, it is evident that the C-O stretches at 1163.11 and 1257.63 cm-1 shifted to 1037.74 and 1253.77 cm-1, the aromatic C=C stretch at 1496.81 cm-1 shifted to 1458.23 cm-1, the C=C stretch at 1687.77 cm-1shifted to 1633.76 cm-1, the C-H stretch at 2966.62 cm-1 shifted to 3333.10 cm-1. These shifts in frequencies suggest that there is interaction between the metal and the inhibitor. The aromatic stretch at 1587.47, the C=O stretch at 1770.71 and the C-H stretch at 2966.62 cm-1 were missing in the spectrum of the corrosion product indicating that these bonds must have been used for adsorption on mild steel surface[23]. In addition, the N-H stretch may also have been used in forming a new bond with the metal.

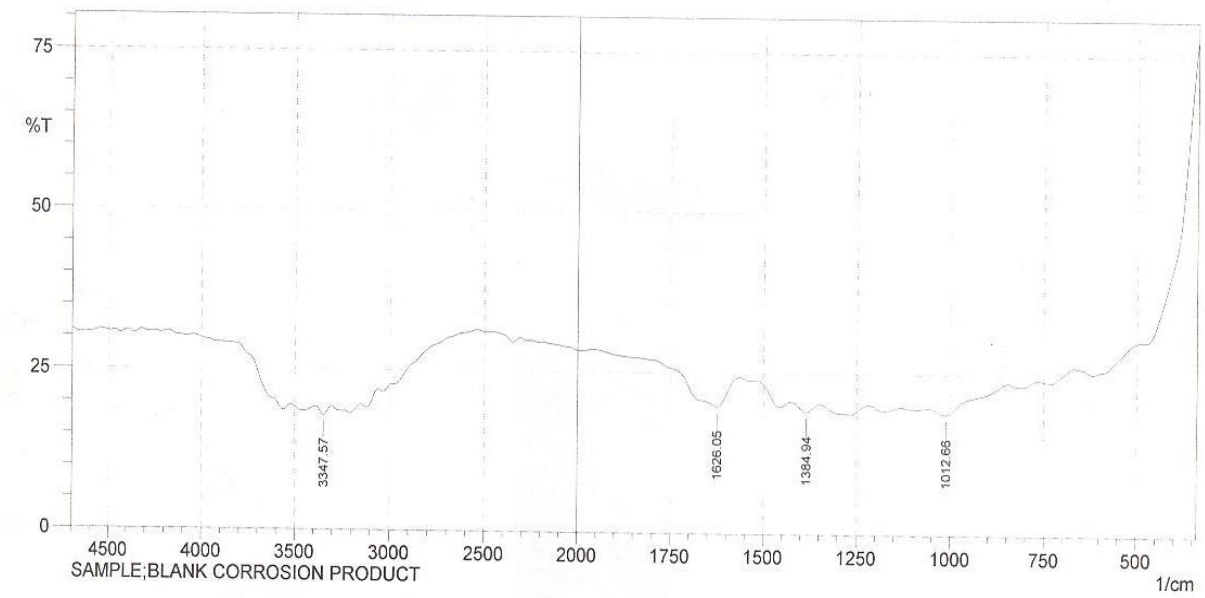


Figure 5: FTIR spectrum of the corrosion product of mild steel in the absence of inhibitor

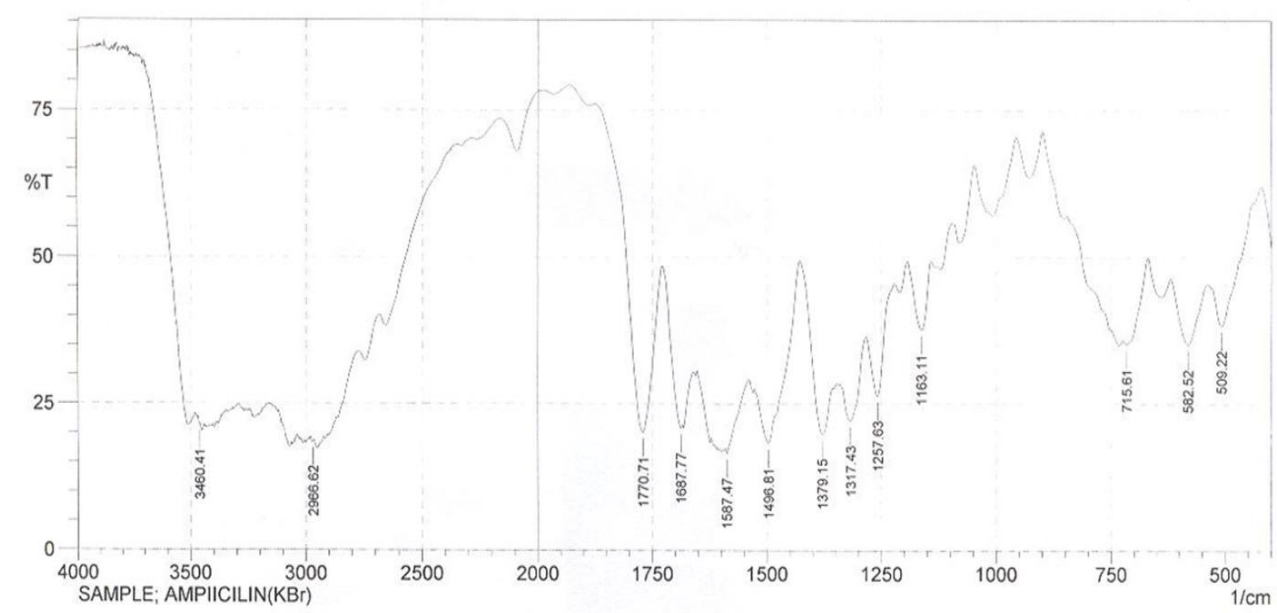


Figure 6: FTIR spectrum of pure sample of ampicillin

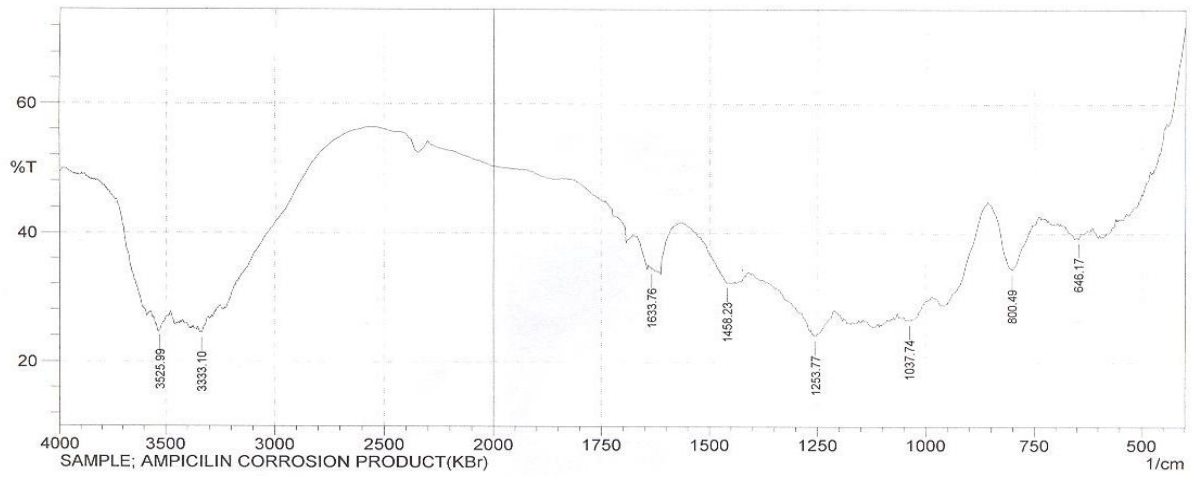


Figure 7: FTIR spectrum of corrosion product of mild steel in the presence of 0.5 g/l of ampicillin

Table 4: Peaks, intensity and assignments of IR adsorption by ampicillin and mild steel corrosion product (containing ampicillin as an inhibitor)

Ampicillin			**Corrosion product**		
Peak (cm^{-1})	**Intensity**	**Assignments**	**Peak (cm^{-1})**	**Intensity**	**Assignments**
1163.11	37.645	C-O stretch	1037.74	26.49	C-O stretch
1257.63	26.35	C-O stretch	1253.77	24.06	C-O stretch
1496.81	18.27	Aromatic C=C	1458.23	32.30	Aromatic C=C
1587.47	16.57	Aromatic C=C			
1687.77	20.81	C=C stretch	1633.76	34.44	C=C bond
1770.71	20.14	C=O stretch			
2966.62	18.57	C-H stretch			
3460.41	21.37	-OH stretch	3333.10	24.47	O-H stretch
			3525.99	24.80	N-H stretch

Density functional theory (DFT)

DFT is based on the principle that the energy of a molecule can be determined from the electron density instead of a wave function. The DFT based on the Hohnenberg-Kohn theorems has been found to be a strong tool for the modelling and development of conceptual issues on chemical reactivity[24]. In corrosion study, DFT has also been found to be a powerful tool that can be used for the prediction of the sites for electrophilic and nucleophilic attacks[25]. The Fukui function provides an avenue for analysing the local selectivity of a corrosion inhibitor. The Fukui function can be defined as equation 10.

$$f(r) = [(\delta\Upsilon/\delta\nu(r))]_N \quad 10$$

where $\nu(r)$ is the external potential and the functional derivative must be taken at constant number of electrons. Assuming $[\delta TE/\delta N]_\nu$ and $[\delta TE/\delta\nu(r)]_N$ are exact differentials, then the Maxwell relations between the derivatives can be written as equation 11.

$$f(r) = [(\delta\rho(r)/\delta N)]_\nu \quad 11$$

According to [26], equation 11 is the most standard presentation of the Fukui function. Owing to the discontinuity of the chemical potential at integer N, the derivative will be different if taken from the right or the left hand side. Therefore three different forms of Fukui functions (f^+, f^0 and f^-) are possible. These correspond to the situation when N increases from N to N+1(f^+) and when N decreases from N to N-1 (f^-). f^+ is associated with the LUMO and measures the reactivity towards a donor reagent while f^- is associated with the HOMO and measures the reactivity toward an acceptor reagent. However, the average of both (f^0) measures reactivity towards a radical. However, in this work, the finite difference approximation was used to calculate the Fukui functions for electrophilic and nucleophilic Fukui function from equations 12 and 13.

$$f^+ = (\delta\rho(r)/\delta N)^+_\upsilon = q_{(N+1)} - q_{(N)} \quad 12$$

$$f^- = (\delta\rho(r)/\delta N)^-_\upsilon = q_{(N)} - q_{(N-1)} \quad 13$$

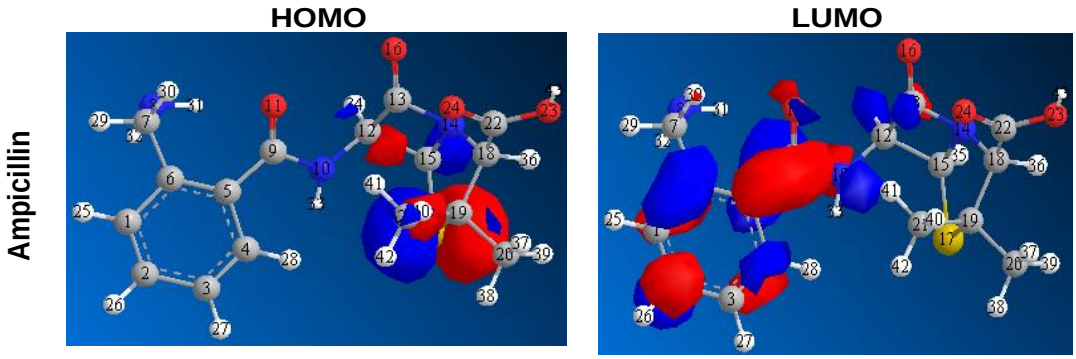
where ρ, $q_{(N+1)}$, $q_{(N)}$ and $q_{(N-1)}$ are the density of electron and the Mulliken/Lowdin charge of the atom with N+1, N and N-1 electrons. Since there is similarity between the Fukui function and the frontier molecular orbitals, it is expected that the site for nucleophilic attack is the site where the value of f^+ is maximum while the site for electrophillic attack is controlled by the values of f^-.

In the ampicillin molecule, several sites are eminent for nucleophilic and electrophilic attacks.

These sites include O10, N9, C11 and C11 while the corresponding sites for electrophilic attack are C12, N13, C17 and C16. The site favoured depends on the energy associated with the adsorption and also on the orientation of the molecule. The information revealed by Fukui analysis is also manifested in the HOMO and LUMO molecular orbitals of the ampicillin compound.

Table 5: Calculated Muliken charges and Fukui functions for ampicillin using B3-LYP exchange correlation

	q_N	q_{N-1}	q_{N+1}	f^+	f^-
C(1)	-4.0000	-3.9321	-0.0278	3.9721	-0.0679
C(2)	-4.0000	-4.0040	0.0076	4.0076	0.0040
C(3)	-4.0000	-3.9933	-0.0124	3.9876	-0.0067
C(4)	-4.0024	-4.6553	0.2532	4.2556	0.6529
C(5)	-4.0051	4.5889	-2.2266	1.7785	-8.5939
C(6)	-4.0002	-2.3956	-0.9097	3.0905	-1.6046
C(7)	-3.3058	4.9309	0.9807	4.2865	-8.2367
N(8)	-4.0019	-4.6270	-3.2771	0.7248	0.6251
C(9)	-2.9662	5.6161	1.3616	4.3278	-8.5823
N(10)	-2.0981	4.2918	0.1326	2.2307	-6.3899
O(11)	3.9631	3.9886	-0.0173	-3.9804	-0.0256
C(12)	4.9866	5.4787	1.0840	-3.9026	-0.4921
C(13)	4.6121	4.0049	-0.0150	-4.6271	0.6072
N(14)	0.3236	4.0771	1.4814	1.1578	-3.7534
C(15)	-2.0000	-1.9965	1.9391	3.9391	-0.0035
O(16)	3.9704	5.2132	0.9890	-2.9814	-1.2428
S(17)	3.9614	2.1274	-0.0916	-4.0530	1.8340
C(18)	3.9680	-4.7542	-1.9246	-5.8926	8.7222
C(19)	4.0723	-4.1906	-0.0726	-4.1449	8.2629
C(20)	4.5184	4.2891	0.1950	-4.3234	0.2293
C(21)	4.1472	-3.9974	0.0935	-4.0537	**8.1446**
C(22)	-2.3969	-2.0000	2.0064	**4.4033**	-0.3970
O(23)	4.2641	-2.0045	1.0257	-3.2384	6.2686



CONCLUSIONS

Ampicillin is a good adsorption inhibitor for the corrosion of mild steel in HCl solutions. The adsorption of the inhibitor on the mild steel surface is exothermic, spontaneous and is consistent with the Langmuir adsorption model. The mechanism of adsorption of the inhibitor on the mild steel is consistent with the mechanism of charge transfer from the inhibitor to the metal surface, which indicates physiosorption. The sites for nucleophilic and electrophilic attacks on the ampicillin molecule are on the (C11) and (C12) bonds respectively.

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