



Amoxicillin as an efficient green corrosion inhibitor for mild steel in 1M sulphuric acid

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Abstract

The corrosion inhibition of mild steel in 1M Sulphuric acid using amoxicillin as inhibitor has been investigated by weight loss, Potentiodynamic polarization, electrochemical impedance spectroscopy, Hydrogen permeation and diffuse reflectance spectroscopic measurements. All these techniques reveal that inhibition efficiency increases with an increase in the concentration of inhibitor. Scanning electron microscopy [SEM] was portrayed for uninhibited and inhibited mild steel surfaces to ascertain the adsorption of inhibitor on the metal. Potentiodynamic polarization studies indicated that inhibitor act as mixed type. Diffuse reflectance spectroscopy and quantum mechanical calculations substantiated the mere adsorption of inhibitor on the mild steel surface which is responsible for corrosion inhibition of steel in 1M Sulphuric acid. The adsorption of the compounds on mild steel surface obeys Langmuir adsorption isotherm.

Keywords: Amoxicillin, Polarization, Permeation, corrosion, inhibitor, adsorption, quantum.

1. Introduction

Mild steel is an important category of metals due to its excellent mechanical properties. Mild steel is extensively used under different conditions in chemical and allied industries in handling acidic, alkaline and salt solutions. Mild steel is used in industries as pipelines for petroleum industries, storage tanks, reaction vessel and chemical batteries¹. Acid solutions are widely used in many industrial processes. Acids are used for acid cleaning, pickling and descaling due to their chemical properties²⁻⁵. In general, the high corrosive nature acids cause damage to the mild steel during pickling. Several methods were used to decrease the corrosion of metals in acidic medium. Among them the use of inhibitors is the most economical and practical method to reduce electrochemical corrosion⁶⁻¹⁰. It has been reported that heterocyclic organic compounds having π bonds and containing hetero atoms such as sulphur, nitrogen, oxygen and phosphorous were reported as corrosion inhibitors by few researchers¹¹⁻¹⁶. The most of the organic inhibitors thus reported are toxic, highly expensive and environmentally unfriendly. Research activities in recent times are geared towards developing the cheap, non-toxic drugs as environmentally friendly corrosion inhibitors¹⁷⁻²⁴.

The careful perusal literature indicates that few antibiotics have been reported as corrosion inhibitors for the corrosion of mild steel and aluminium in acidic and alkaline media²⁵. Recently, the use of amoxycillin as an inhibitor for the corrosion of mild steel in 1 M HCl was reported by Hari Kumar et al²⁶. However no concrete report is available for the corrosion inhibition of mild steel in 1M sulphuric acid employing Amoxicillin as an inhibitor. The quantum chemical parameters for Amoxicillin are reported first time here to give the effect of molecular structure on the chemical reactivity.

The inhibition efficiencies of the compound were screened using weight loss, electrochemical techniques. Seldom had the use hydrogen permeation measurements and diffuse reflectance studies for this antibiotic confirmed the impressive performance of the inhibitor. The compound is large and amply planar to block more surface area on the mild steel.

2. Experimental section

2.1. Materials

Mild steel specimens of size 1×4 cm² were used for weight loss and electrochemical studies. 1 M H₂SO₄, AR Grade was used for all the studies. The antibiotic (amoxicillin) was procured from the alkem laboratories limited. The structure of the antibiotic is shown in Figure 1. Electrochemical experiments were performed using a three

electrode cell assembly with mild steel samples as working electrode, platinum as counter electrode and Hg/Hg₂SO₄/1M H₂SO₄ as the reference electrode.

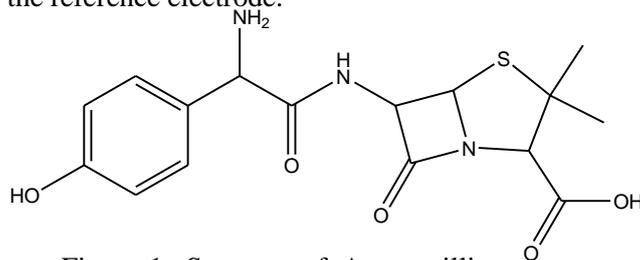


Figure 1 Structure of Amoxicillin

2.2. Weight loss studies

Weight loss and hydrogen permeation studies were carried out as described earlier²⁷. The concentrations of inhibitor used for weight loss and electrochemical study were from 5×10^{-4} M to 15×10^{-4} M. Mild steel specimens of size 1×4 cm² were abraded with different emery papers and then degreased with acetone. The cleaned samples were then washed with double distilled water, finally dried and kept in the desiccator. The weight loss study was carried out at room temperature for three hours in 1 M H₂SO₄. The inhibition efficiency (IE %) was determined by the following equation:

$$\text{Inhibition Efficiency (IE \%)} = (W_0 - W_i / W_0) \times 100 \quad (1)$$

Where W_0 & W_i are the weight loss values in absence and presence of the inhibitor.

2.3. Electrochemical studies

Potentiodynamic polarization measurements were carried out in EG&G Princeton Applied research 7310 at a scan rate of 10 mV s⁻¹. Before recording the polarization curves the solution was deaerated for 20 min. and the working electrode was maintained at its open circuit potential for 10 minutes. The mild steel surface was exposed to various concentrations of inhibitor in 100 mL of 1 M H₂SO₄ at room temperature. The inhibition efficiency (IE %) was calculated using the equation:

$$\text{Inhibition Efficiency (IE \%)} = (I_0 - I / I_0) \times 100 \quad (2)$$

Where I_0 and I are the corrosion current density without and with the inhibitor respectively.

The potentiodynamic current-potential curves were recorded by changing the electrode potential from -750 mV to +750 mV versus the open circuit potential. The corresponding corrosion current (I_{corr}) was recorded. Tafel plots were constructed by plotting E versus log I. Corrosion Potential (E_{corr}), corrosion current density (I_{corr}) and cathodic and anodic slopes (β_c and β_a) were calculated according to known procedures.

Impedance measurements were carried out in the frequency range from 0.1 to 10000 Hz using amplitude of 20 mV and 10 mV peak to peak with an AC signal at the open-circuit potential. Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were obtained from Nyquist plot²⁸⁻³⁰. The percentage inhibition efficiency was calculated from the equation:

$$\text{Inhibition Efficiency (IE \%)} = (R_{\text{ct}} - R'_{\text{ct}} / R_{\text{ct}}) \times 100 \quad (3)$$

Where R'_{ct} and R_{ct} are the charge transfer resistance of mild steel with and without inhibitor respectively.

2.4. Hydrogen permeation studies

The hydrogen permeation study was carried out using an adaptation of modified Devanathan and Stachurski's, two compartment cell as described elsewhere³¹. The hydrogen permeation current was obtained in the absence and presence of inhibitor used in the present study.

2.5. Surface Morphology

The Scanning electron microscopy (SEM) was portrayed to examine the specimen's surface which is immersed in both inhibited [for the concentration 15×10^{-4} M of antibiotics] and uninhibited solutions. The

surfaces of corroded and corrosion inhibited mild steel specimens were examined by diffuse reflectance studies in the region 200- 700 nm using U-3400 spectrometer [UV-VIS-NIR Spectrometer, Hitachi, Japan].

2.6. Theoretical Calculations

Quantum chemical calculations were carried using Gaussian 03 Software. All theoretical quantum calculations were carried with full geometry optimizations using program default calculation settings. The energy of highest occupied molecular orbital (E_{HOMO}), lowest unoccupied molecular orbital (E_{LUMO}), Dipole moment (μ) and total energy of the molecule were calculated with the above given software package.

3. Results and discussion

3.1. Weight loss studies

The values of inhibition efficiency (IE %), corrosion rate (CR) and surface coverage (θ) calculated for amoxicillin in 1 M H_2SO_4 at different concentrations from the weight loss data is summarized in the Table 1. It is evident from the table that inhibition efficiency increases with increase in the inhibitor concentration. It is also observed that corrosion rate decreases with increase in inhibitor concentration. Maximum inhibition efficiency is observed at 15×10^{-4} M concentrations of the inhibitor. Beyond this concentration, the inhibition efficiency decreases due to desorption of inhibitor from the mild steel surface.

Table 1: Values of Inhibition Efficiency, Corrosion rate and Surface coverage for the corrosion of mild steel in 1 M H_2SO_4 in presence of different concentrations of Amoxicillin obtained from weight loss measurements

Inhibitor Conc. (M)	Weight Loss (g)	Inhibition Efficiency (%)	Corrosion Rate (mg $cm^{-2}h^{-1}$)	Surface Coverage (θ)
Blank	0.0809	-	6.74	-
5×10^{-4}	0.0417	44.11	3.44	0.4411
10×10^{-4}	0.0312	57.78	2.60	0.5778
15×10^{-4}	0.0247	66.57	2.05	0.6657
20×10^{-4}	0.0407	49.69	3.68	0.4969

3.2. Potentiodynamic polarization studies

Polarization curves for mild steel in 1 M H_2SO_4 containing different concentrations of inhibitor are given in Figure 2. The values of corrosion potential (E_{corr}), corrosion current densities (I_{corr}), anodic tafel slope (β_a), cathodic tafel slope (β_c), surface coverage (θ) and inhibition efficiency (IE%) calculated using Potentiodynamic polarization are summarized in Table 2.

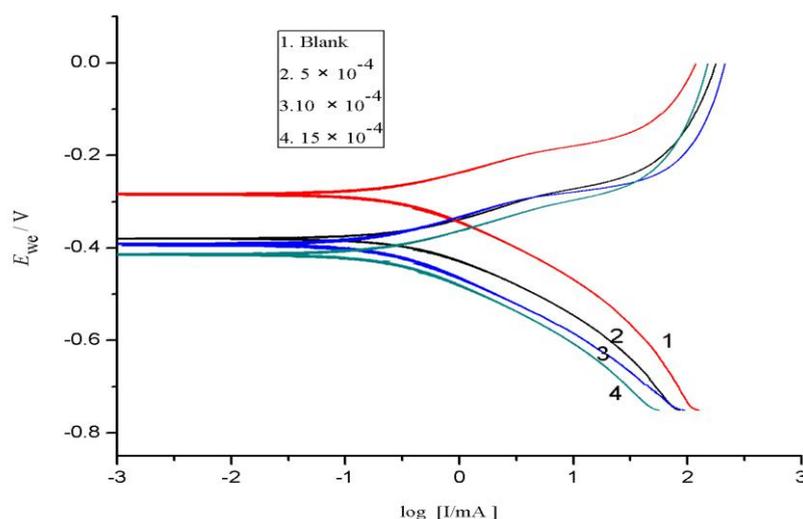


Figure 2 Polarization curves of mild steel in 1 M H_2SO_4 at different concentrations of Amoxicillin

The corrosion current (I_{corr}) value decreases with increase in the concentration of the inhibitor. Further it is ascertained that increasing concentrations of antibiotic decreases the values of both β_a and β_c , in indefinite fashion indicating the performance of inhibitor is under mixed control. The inhibition efficiency (IE %) and surface coverage (θ) increases with increase in inhibitor concentration. The maximum inhibition efficiency is achieved at 15×10^{-4} M concentration. A definite correlation exists between the results obtained from weight loss and polarization studies.

Table 2 Electrochemical parameters and Inhibition Efficiency for corrosion of mild steel in 1 M H_2SO_4 obtained by Polarization method in presence different concentrations of Amoxicillin

Inhibitor Conc. (M)	E_{corr} (mV)	I_{corr} ($\mu A\ cm^{-2}$)	β_a (mV dec^{-1})	β_c (mV dec^{-1})	IE (%)	Surface Coverage (θ)
Blank	376.12	548.57	82.9	135.3	-	-
5×10^{-4}	-378.91	335.71	79.5	131.0	38.80	0.3880
10×10^{-4}	-411.19	273.35	68.9	128.0	50.17	0.5017
15×10^{-4}	-427.28	208.35	61.4	121.3	62.01	0.6201

3.3. Electrochemical impedance studies

The nyquist representations of impedance behavior of mild steel in 1 M H_2SO_4 with and without addition of different concentrations of inhibitor are shown in Figure 3. At all concentration range of inhibitors one large capacitive loop at higher frequency range was acquired and the diameter of the circle increased with increase in inhibitor concentration. The higher frequency capacitive loop might be due to the adsorption of inhibitor molecule

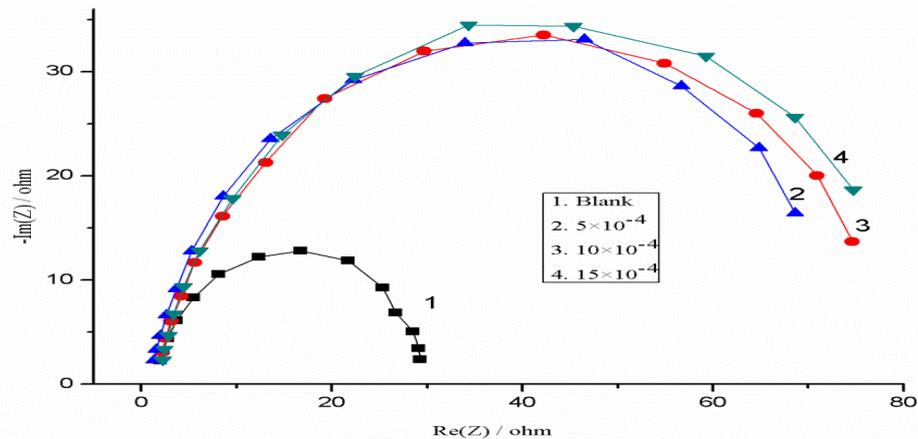


Figure 3 Nyquist plot for mild steel in 1 M H_2SO_4 containing different concentrations of Amoxicillin

Table 3 indicates that the values of R_{ct} are found to increase with increase in concentration of the compound in the acid while C_{dl} are brought down by increasing concentrations of inhibitor in the acid medium. This can be attributed to increasing adsorption of the compound on metal surface.

Table 3 Electrochemical parameters and Inhibition efficiency for corrosion of mild steel in 1 M H_2SO_4 obtained by Impedance method in presence of different concentrations of Amoxicillin

Inhibitor Conc. (M)	R_{ct} ($\Omega\ cm^2$)	C_{dl} ($F\ cm^{-2}$)	IE (%)	Surface Coverage (θ)
Blank	28.1	0.489	-	-
5×10^{-4}	54.16	0.412	48.11	0.4811
10×10^{-4}	66.39	0.385	57.67	0.5767
15×10^{-4}	91.98	0.367	69.14	0.6914

3.4. UV spectral reflectance studies

The corrosion inhibition of mild steel in 1 M H₂SO₄ in the presence of inhibitor may be due to the formation of a thin film on the surface of the metal surface. This is supported by the reflectance studies carried out using spectrophotometer with different mild steel specimens. A reflectance curves for polished specimen, specimen dipped in blank solution and in inhibitor was shown in Figure 4.

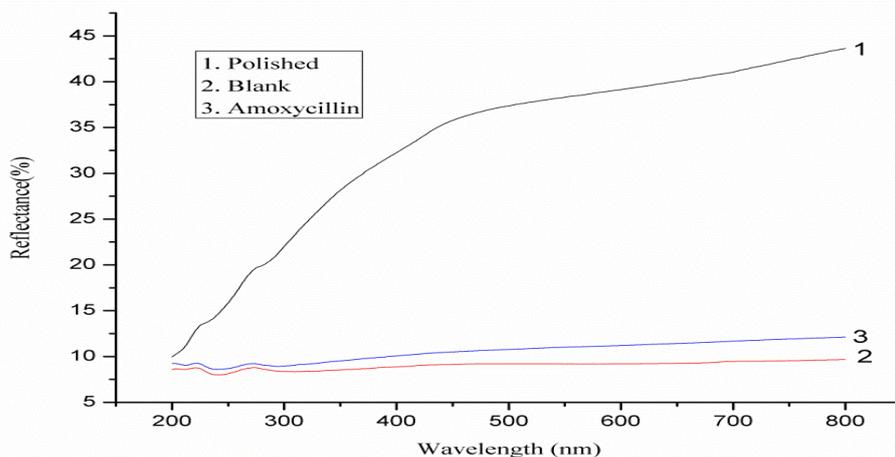


Figure 4 UV Reflectance curves of mild steel in 1 M H₂SO₄ with 15x10⁻⁴M of the inhibitor.

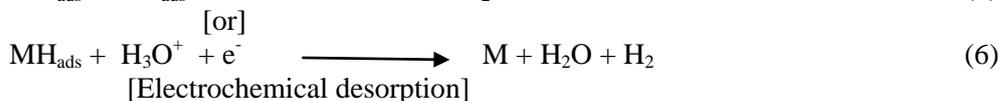
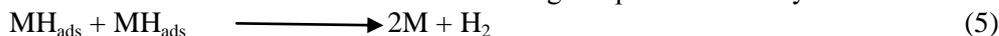
This study indicates that the percentage of reflectance is maximum for polished mild steel and it gradually decreases for the specimen dipped in 1 M H₂SO₄ solution. This observation reveals that the change in surface characteristic is due to the corrosion of mild steel. The reflectance percentage of inhibitor used specimens are higher than the blank one. This confirms that the surface characteristics are not altered more due to the formation of a film on the surface. The reflectance percentage increased as the concentration of inhibitor increased due to the increase in adsorption of the inhibitor.. Similar observation has been made by Madhavan et al.³³.

3.5. Hydrogen permeation measurements

Hydrogen can enter into the metal during various industrial operations like melting, heat treatment, or pickling and electrochemical processes such as cathodic cleaning and electrolytic machining. Of the various sources of entry of hydrogen into the metal, pickling is one of the basic steps in electroplating processes in which mineral acids are used for the removal of rust and scale. The following are the main reactions in acidic solutions.



Where ‘M’ is the cathodic metal surface. This discharge step is followed by either



A part of the atomic hydrogen liberated during the pickling process enters the metal, and the remainder is evolved as hydrogen gas. Organic compounds are generally added to pickling baths in order to minimize the base metal attack and limit the hydrogen liberated. However, the fraction of hydrogen atoms that enters the metal produces some detrimental effects³⁴ on the mechanical properties of iron/steel, such as reduction in ductility, lowering of fracture stress and loss in mechanical strength leading to embrittlement. This phenomenon is also called ‘delayed failure’. It has been already pointed out that hydrogen permeation current measurement, under pickling conditions, can be a useful tool for evaluating inhibitors from the point of view of predicting the extent of hydrogen embrittlement. A similar suggestion has been made with regard to the screening of additional agents employed in electroplating baths for their capacity to decrease hydrogen intake.

In the present study the hydrogen permeation currents are recorded in H₂SO₄ in the absence and presence of inhibitor. This study has been taken up with an idea of screening the inhibitor with regard to their effectiveness on the reduction of hydrogen uptake. The values of permeation current with respect to time are given in Table 4. Figure 5 shows the variation of permeation current vs time for mild steel in 1 M H₂SO₄ in the presence Amoxicillin.

Table 4 Values of permeation current for mild steel in 1 M H₂SO₄ and in presence 15x10⁻⁴M Amoxycillin with respect to change in time.

Time (min.)	Permeation Current (μA)	
	1 M H ₂ SO ₄	Amoxycillin
0	10.8	4.0
5	11.2	4.7
10	12.0	5.2
15	12.3	5.6
20	12.9	6.1
25	12.9	6.1
30	12.9	6.1
35	12.9	6.1
40	12.9	6.1

From fig.5, it is evident that the compound brings down the permeation current to the extent of 50%. The corrosion inhibition efficiency of the compound in 1 M H₂SO₄ follows the same order. Thus a definite correlation exists between the corrosion inhibition efficiency and the extent of reduction in the permeation current of this compound. It is a well-known fact that the higher the cathodic Tafel slope in the presence of an inhibiting compound, the lesser is the corrosion and hydrogen intake by the metal. An increase in the cathodic Tafel slope leads to increase in the energy barrier for proton discharge and decrease in the evolution of hydrogen. This in turn leads to lower permeation of hydrogen through the metal.

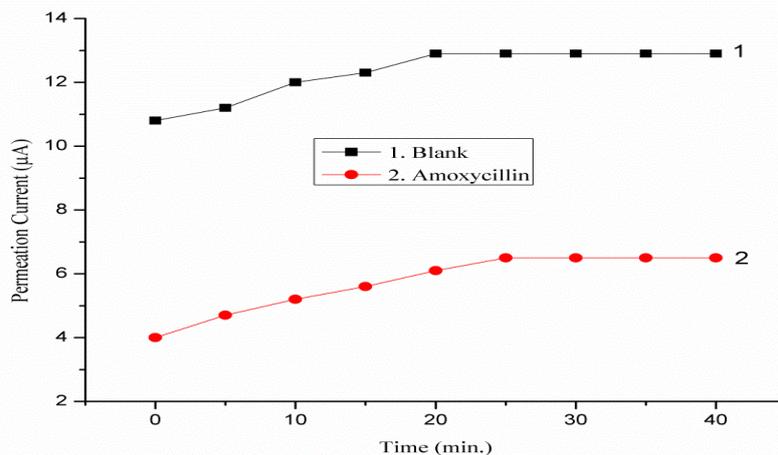


Figure 5 Hydrogen permeation Vs Time curves for mild steel in 1 M H₂SO₄ and 15x10⁻⁴ M concentration of inhibitor

3.6. Adsorption isotherm

The degree of Surface Coverage (θ) for different concentrations of inhibitor in 1 M H₂SO₄ has been calculated from weight loss, Polarization and Electrochemical Impedance studies. The obtained data was tested graphically for fitting suitable isotherm^{35, 36}. Almost a straight line was obtained by plotting $\log(C/\theta)$ Vs $\log C$ shown in Figure 6, which proves that the adsorption of the compound obeys Langmuir adsorption isotherm.

The Langmuir isotherm for the adsorbed layers is given by the equation³⁷,

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad (7)$$

Where K_{ads} is the equilibrium constant of the adsorption/desorption process. Adsorption equilibrium constant (K_{ads}) and free energy of adsorption [ΔG°_{ads}] were calculated using the equation³⁸

$$K_{ads} = 1/C_{inh} \times \theta / 1-\theta \quad (8)$$

$$\Delta G^{\circ}_{ads} = -2.303RT \log [55.5K_{ads}] \quad (9)$$

Where 55.5 is the molar concentration of water in solution³⁹. R is the gas constant, T is the temperature. The values of adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG°_{ads}) are given in Table 5. The negative values of (ΔG°_{ads}) indicated that adsorption of inhibitors is a spontaneous process. It is known that the values of (ΔG°_{ads}) are of order -20 kJmol⁻¹ or lower indicates a physisorption, those of the order of -40 kJmol⁻¹ or higher involve charge sharing or transfer from the inhibitors to the metal surface to form a co-ordinate bond, the process known as chemisorption⁴⁰⁻⁴². The values of free energy of adsorption (ΔG°_{ads}) in this study lies in the

range -25 to -28 kJ mol⁻¹, indicating that the adsorption is not a simple physisorption but it may involve some other interactions⁴³.

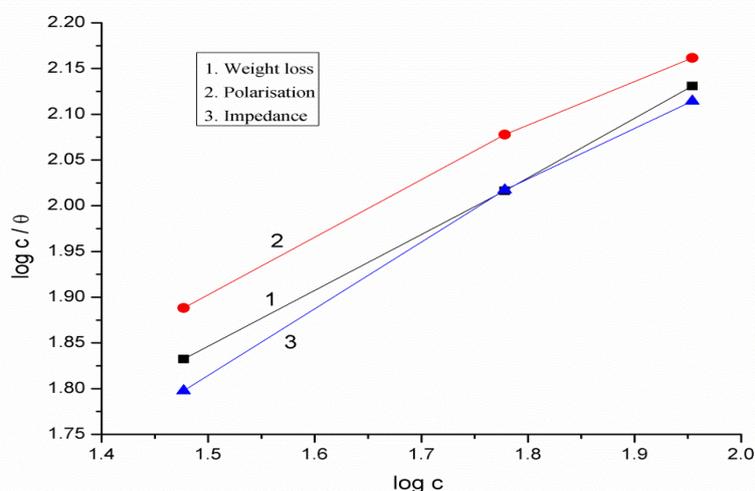


Figure 6 Langmuir's adsorption isotherm plots for the adsorption of Amoxicillin in 1 M H₂SO₄ on the steel surface.

Table 5 Gibbs free energy parameters and adsorption equilibrium constant (K_{ads}) of Amoxicillin inhibitor at various temperatures evaluated by weight loss method

Temperature [K]	K_{ads}	$-\Delta G^{\circ}_{ads}$ [kJ mol ⁻¹]
313	289	25.19
323	427	27.05
333	481	28.21

3.7. Scanning electron microscopic studies

SEM photographs obtained for mild steel surface immersed in 1 M H₂SO₄ solutions for 3 hrs in the absence and presence of the inhibitor are shown in Figure 7 [A&B]. It is apparent that the specimen surface is strongly damaged in the absence of the inhibitor. SEM image of inhibited mild steel specimen (B) reveals that a good protective adsorbed film is formed on the specimen's surface, which suppresses the rate of corrosion, being responsible for the inhibition.

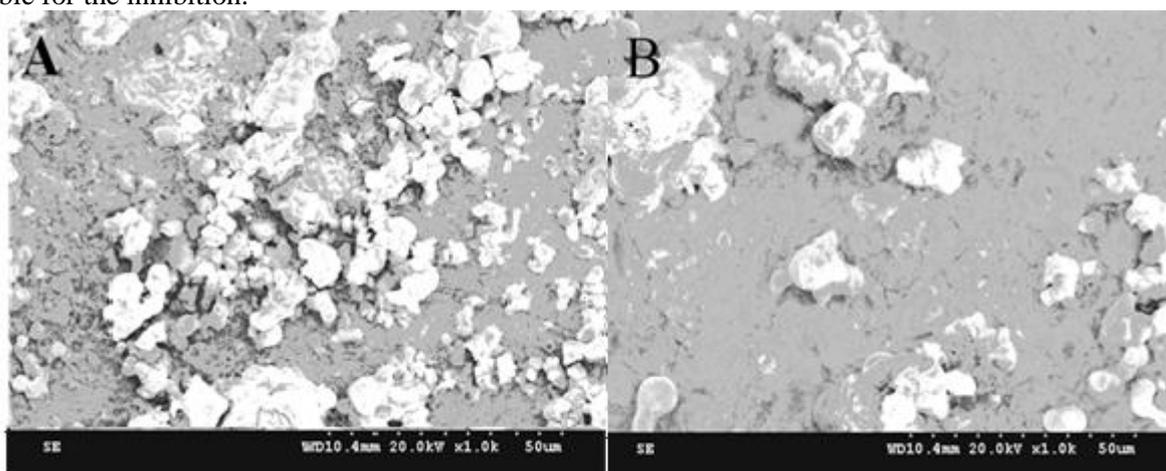


Figure 7 SEM images of mild steel [A] immersed in 1 M H₂SO₄, [B] 15 x 10⁻⁴M Amoxicillin for 3h

3.8. Quantum chemical calculations

Quantum chemical calculations were carried out to investigate the adsorption and inhibition mechanism of the inhibitor. Figure 8 shows the optimized structure of Amoxicillin. The values of calculated quantum chemical parameters i.e. E_{HOMO} (highest occupied molecular orbital), E_{LUMO} (lowest unoccupied molecular orbital), ΔE (energy gap), μ (dipole moment), etc., are summarized in Table-6.

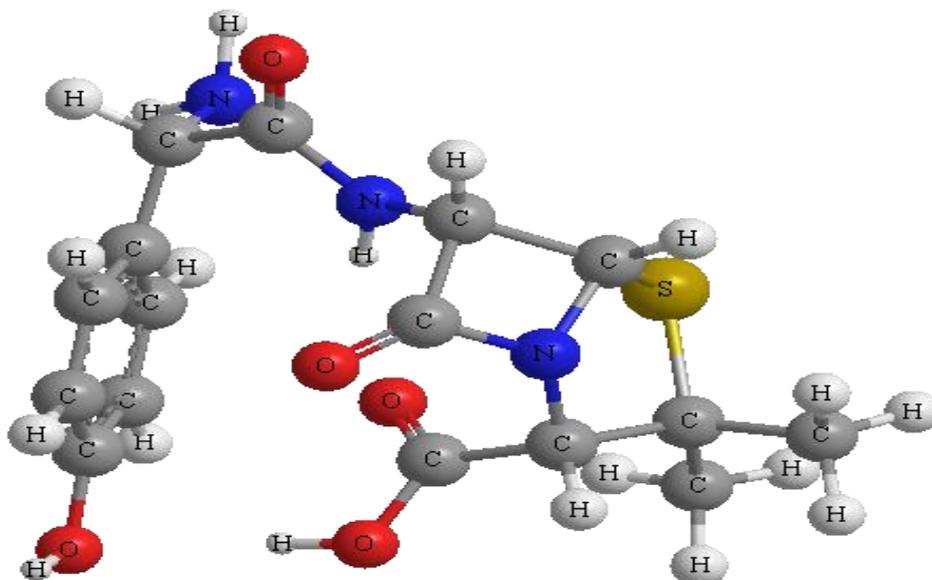


Figure 8 Optimised structure of Amoxicillin

E_{HOMO} is associated with the electron-donating ability of the molecule. Several researchers have shown that the adsorption of an inhibitor on metal surface can occur on the basis of donor-acceptor interactions between the π -electrons of heterocyclic atoms and the vacant d-orbital's of the metal surface atoms⁴⁴⁻⁴⁶. A high value of E_{HOMO} indicates a tendency of a molecule to donate electrons to acceptor molecules with low energy empty molecular orbital. Increasing values of E_{HOMO} facilitates the adsorption and increases the inhibition efficiency by influencing the transport process through the adsorbed layer⁴⁷. E_{LUMO} indicates the ability of the molecule to accept the electrons, hence these are acceptor states. The lower the value of E_{LUMO} , the more probable is that the molecule can accept electrons and increase the inhibition efficiency. Regarding ΔE ($E_{\text{LUMO}}-E_{\text{HOMO}}$) lower values of energy difference will cause higher inhibition efficiency because energy to release electron from last occupied orbital will be low. When dipole moment is concerned higher values of μ , will favour a strong interaction of inhibitor molecule with the metal surface^{48,49}.

In the present study the LUMO values of amoxicillin is lower and HOMO is higher, Further the lower dipole moment and higher total energy values signify the strong interaction of amoxicillin with the metal leading to the better adsorption of the compound on steel surface.

Table 6 Calculated quantum chemical parameters of Amoxicillin

Parameter	Amoxicillin
E_{HOMO} , eV	-8.474
E_{LUMO} , eV	0.454
ΔE , eV	8.928
μ (debye)	2.3972
Total Energy, (kcal.mol ⁻¹)	50.5928

Figure 9 (A) points out that highly occupied molecular orbitals (HOMO) are localized on hetero atoms where as in Figure 9 (B) the lowest unoccupied molecular orbital's are localized on the aromatic carbons of the benzene ring. From both the figures it can be observed that HOMO localized centers are higher than the LUMO localized centers leading to the higher HOMO energy and hence superior adsorption of the compound on steel surface.

3.9. Mechanism of inhibition

Corrosion inhibition mechanism in acidic medium is based on the adsorption of inhibitor on the metal surface. The process of adsorption is influenced by the nature and charge of the metal, chemical structure of the inhibitor and the type of the aggressive electrolyte.

Potential of zero charge (pzc) on the correlative scale (ϕ_c) is used to determine the charge of the metal surface immersed in the electrolyte^{50,51} using the equation,

$$\phi_c = E_{\text{corr}} - E_{q=0}$$

where, $E_{q=0}$ is potential of zero charge. The potential of zero charge (pzc) for iron in H_2SO_4 solution was found to be -550mV vs SCE (Saturated Calomel Electrode) ⁵². The values of E_{corr} obtained for blank and different concentrations of inhibitor medium are -376, -378, -411 and -427 respectively. By substituting these values in the above equation the values of ϕ_c are +174, +172, +139, and +123 vs $\text{Hg}/\text{HgSO}_4/1\text{M } \text{H}_2\text{SO}_4$ respectively. From the positive values of ϕ_c it is confirmed that metal surface is highly positive charged.

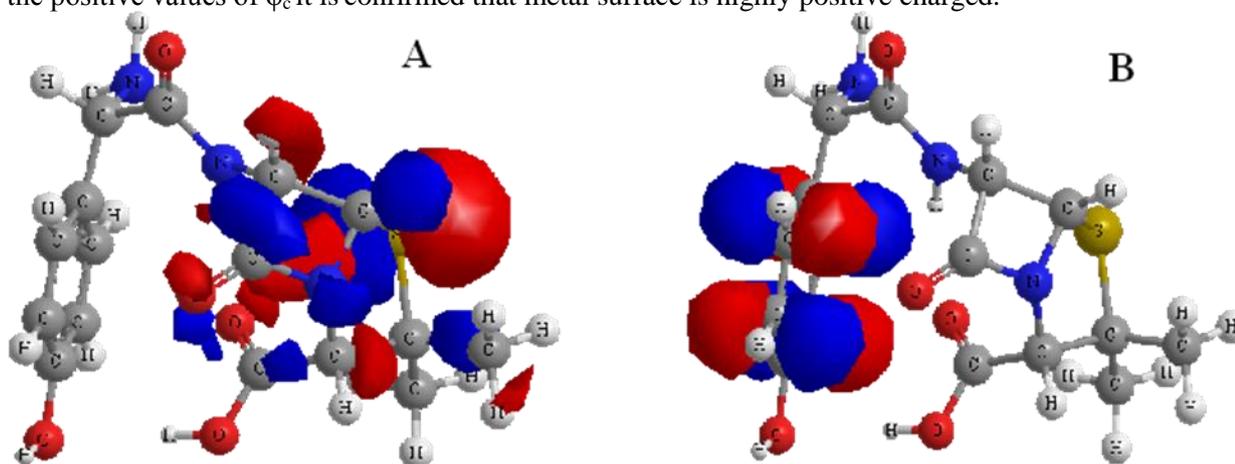


Figure 9 Frontier molecular orbital density distributions of Amoxicillin: (A) HOMO (B) LUMO

In amoxicillin the -OH group gets protonated and the species becomes as a protonated species. When the mild steel is dipped in the acid the positively charged surface of the steel becomes negatively charged due to the adsorption of negatively charged sulphate ions of the acid. Now the protonated species gets easily adsorbed on the negatively charged surface.

Some free amoxicillin molecules get adsorbed on the metal surface through π -electrons of the aromatic ring, unshared pair of electrons from N,S & O and vacant d-orbital's of the metal surface.

4. Conclusions

The corrosion rates of mild steel were monitored and controlled in 1 M H_2SO_4 solutions without and with various concentrations of Amoxicillin by adapting chemical and electrochemical methods. The eco friendly inhibitor retards the dissolution of mild steel in 1M H_2SO_4 . Tafel polarization plots indicated that the compound act as mixed- type inhibitors. Rates of corrosion obtained from the impedance measurements were in good agreement with those recorded using the Tafel polarization plots. This confirms the validity of the corrosion rates measured by the Tafel polarization plots.

Adsorption of the tested inhibitor was found to obey Langmuir isotherm. The hydrogen permeation measurements confirmed that the inhibitor does not encourage hydrogen embrittlement in steel. Diffuse reflectance spectra and SEM images reveal there is no significant changes in surface morphology by inhibitive action as the compound simply adsorb on the mild steel surface. Quantum mechanical parameters substantiate the mere adsorption of the compound on metal surface. Apparent activation energies in the presence of inhibitor lie in the range -25 to -28 kJmol^{-1} , indicating that the adsorption is not a simple physisorption.

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