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Use of Glutamine as a New and Effective Corrosion Inhibitor for Mild Steel in 1 M HCl Solution

Ambrish Singh[1,*], *Eno E. Ebenso*[2,3]

[1] Department of Chemistry, School of Civil Engineering, LFTS, Lovely Professional University, Phagwara, Punjab, India.
[2] Department of Chemistry, School of Mathematical & Physical Sciences, North-West University(Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
[3]Material Science Innovation & Modelling (MaSIM) Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
[*]E-mail: vishisingh4uall@gmail.com; ambrish.16752@lpu.co.in

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Glutamine was investigated as corrosion inhibitor for mild steel (MS) in 1 M HCl solution by weight loss and quantum chemical calculations. Glutamine showed 96% inhibition efficiency even at very low concentration of 100 ppm. The adsorption of the inhibitor follows Langmuir adsorption isotherm. The quantum chemical calculations were applied to elucidate adsorption pattern of inhibitor molecules on steel surface.

Keywords: Glutamine, Mild steel, Weight loss, Adsorption, Quantum chemical measurements.

1. INTRODUCTION

Acid solutions, especially hydrochloric and sulfuric acids, are widely used in various industrial processes, such as pickling of iron, chemical cleaning, descaling of boilers, and oil well acidification in petroleum exploration. The use of inhibitors is one of the most practical methods for corrosion protection of metallic objects in acidic media, as well as for reduction of acid consumption occurring during the course of corrosion. The corrosion for metals and alloys is a problem of serious concern which considerably affects both economy and safety. Steel is widely used in industries and machinery and many other fields [1]. Inhibitors are used in acid solution to prevent metal dissolution. The use of organic inhibitors is most effective and most economic method for protection of metallic corrosion.

The efficiency of an organic compound as an inhibitor depends on its ability to get adsorbed on the metal surface by replacing water molecule from metal surface [2].

Generally the compounds containing hetero atoms like O, N, S, and P are found to work as very effective corrosion inhibitors. The efficiency of these compounds depends upon electron density present around the hetero atoms, the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption, and formation of metallic complexes [3-6].

Amino acids are non-toxic, relatively cheap, and easy to produce with purities greater than 99%. They are considered to be more promising green inhibitors [7]. Amino acid compounds were reported to show corrosion resistant behaviour on copper, mild steel and aluminium alloy [8-14]. We observed that the amino acid act as efficient corrosion inhibitors due to the presence of π electrons, hetero atoms in their molecules through which they are either adsorbed or form insoluble metal complex at the metal surface and inhibit metal corrosion [15]. Glutamine amino acid is one of the 20 amino acids encoded by the standard genetic code. It is not recognized as an essential amino acid, but may become conditionally essential in certain situations, including intensive athletic training or certain gastrointestinal disorders. In present work we have investigated the inhibition action of Glutamine as corrosion inhibitor of mild steel in 1 M HCl using weight loss and quantum chemical calculations.

2. EXPERIMENTAL

2.1. Materials

All the tests were performed on mild steel of following composition (wt. %): 0 .076% C, 0.192% Mn, 0.012% P, 0.026% Si, 0.050% Cr, 0.023% Al, 0.123% Cu and bal. Fe. Specimens with dimensions of 2.5 cm × 2 cm × 0.025 cm were used for weight loss studies.

2.2. Inhibitor

Glutamine was purchased from the store under the brand name Prolab. The compound is in its purest state, having molecular formula ($C_5H_{10}N_2O_3$) and melting point (180-185 $^{\circ}$C). Its chemical structure is shown in Figure 1. All the concentrations of the inhibitor in acid solution, were taken in ppm (parts per million).

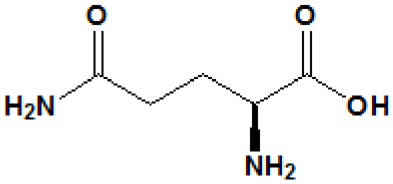

Figure 1. Molecular structure of Glutamine [2-Amino-4-carbamoylbutanoic acid].

2.3. Weight loss measurements

The mild steel specimens used had a rectangular shape of (2.5 cm ×2.0 cm ×0.025 cm) were abraded with series of emery paper (600-1200 grades) and then washed with distilled water and finally with acetone. After weighing accurately, the specimens were immersed in conical flask which contained 100 ml of 1 M HCl in the absence and presence of different concentration of inhibitor. All the test solutions were kept in a thermostated water bath. After 3 h, the specimens were taken out, washed, dried and weighed accurately. The mean corrosion rate (expressed in mg cm^{-2}) with respect to acid and inhibitor was calculated. All the tests were repeated at different temperatures. The corrosion rate (C_R) was calculated from the following equation

$$C_R\,(\mathrm{mm/y}) = \frac{87.6W}{atD} \qquad (1)$$

where W is the average weight loss of mild steel specimens, a total area of one mild steel specimen, t is the immersion time (3 h) and D is density of mild steel in (gcm^{-3}). The inhibition efficiency (η%) of inhibitor on the corrosion of mild steel was calculated as follows,

$$\eta\% = \frac{C_R - {}^{inh}C_R}{C_R} \times 100 \qquad (2)$$

where C_R and ${}^{inh}C_R$ are the corrosion rates of mild steel in the absence and presence of the inhibitors, respectively.

2.4. Quantum chemical calculations

Quantum chemical calculations were performed using density function theory (DFT) method, B3LYP with electron basis set 6-31G* (d, p) for all atoms. All the calculations were executed with Gaussian 03, E .01.The following quantum chemical indices namely energy of HOMO, LUMO, and dipole moment (μ) was determined [16].

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

The weight loss results obtained for mild steel in 1 M HCl in the presence and absence of different concentration of Glutamine are shown in Figure 2a. The corrosion rate (mg cm^{-2}) values of mild steel in 1 M HCl decreases as the concentration of inhibitor increases i.e. the inhibition efficiency increases as the concentration of inhibitor is raised are summarized in Table 1. Further increase in glutamine concentration did not cause any significant change in the performance of the extract.

Table 1. Weight loss measurements for mild steel in 1 M HCl at different concentrations of Glutamine

Inhibitor concentration (ppm)	**Weight loss (mg cm^{-2})**	**η%**	**C_R (mm/y)**	**θ**
Blank	20.0	-	74.2	-
25	3.6	85	13.3	0.82
50	3.1	84	11.4	0.84
75	1.9	90	6.3	0.90
100	0.8	96	2.7	0.96

3.1.2 Effect of immersion time

The variation of inhibition efficiency with immersion time in HCl is shown in Figure 2b. It is found that inhibition efficiency increased with time in HCl. The result indicated that the film formed on the surface of mild steel attributed to good inhibition efficiency.

3.1.4 Effect of temperature

In order to evaluate the adsorption of glutamine and activation parameters of the corrosion process of steel in acidic media, weight loss measurements were carried out in the range of temperature 308-338 K, as shown in Figure 2c, in the absence and presence of glutamine at an optimum concentration during 3 h immersion time. At an optimum concentration of inhibitor the η% decreases with increasing temperature. This is due to increased rate of the dissolution process of mild steel and partial desorption of the inhibitor from the metal surface [17].

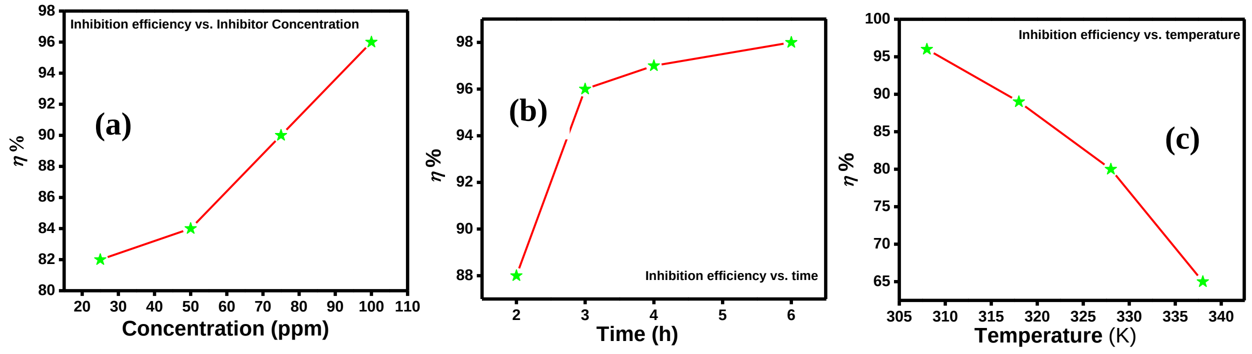

Figure 2. Variation of inhibition efficiency in 1 M HCl on mild steel with (A) different concentrations (25, 50, 75, 100) of Glutamine ; (B) different immersion time (2 hr, 3 hr, 4 hr, 8 hr); (C) different temperatures (308 K, 318 K, 328 K, 338 K) from the weight loss data.

The log of corrosion rate is a linear function with 1/T (Arrhenius equation) [18, 20]:

$$\log C_{\mathrm{R}} = -\frac{E_{\mathrm{a}}}{2.303RT} + \lambda \qquad (3)$$

where, E_a is the apparent effective activation energy, R the general gas constant and λ Arrhenius pre exponential factor. A plot of log of corrosion rate obtained by weight loss measurement versus 1/T gave a straight line as shown in Figure 3a with a slope of -E_a / 2.303R. The values of activation energy are listed in Table 2.

The data showed that the thermodynamic activation functions (E_a) of the corrosion in mild steel in 1 M HCl solution in the presence of glutamine are higher indicating that extract exhibit low η% at elevated temperatures [21-24].

$$k = (\mu RT / Nh)\exp(-\Delta G^{*}/RT) \qquad (4)$$

Where, k is the constant rate and μ the transmission coefficient which represents a distance and can take a value from zero to unity. If we suppose that the corrosion rate is proportional to the constant rate, the alternative formulation of Arrhenius equation is

$$C_R = (\mu' RT / Nh)\exp(\Delta S^{*}/R)\exp(-\Delta H^{*}/RT) \qquad (5)$$

where h is plank's constant, N Avogadro's Number, ΔS^* the entropy of activation, and ΔH^* the enthalpy of activation and $\mu'=B\mu$ (B is the coefficient of proportionality). A plot of log C_R/T versus 1/T gave a straight line (Figure 3b) with a slope of -ΔH^* /2.303R from which the value of ΔH^* was calculated and listed in Table 2. The positive signs of enthalpy (ΔH^*) reflect the endothermic nature of dissolution process [25]. The heat of adsorption (ΔQads) was obtained from the surface coverage and temperature by using following equation,

$$Log\left(\frac{\theta}{1-\theta}\right) = LogA + LogC_{inh} - \left(\frac{\Delta Q_{ads}}{2.303RT}\right) \qquad (6)$$

A plot of $Log\left(\frac{\theta}{1-\theta}\right)$ vs $1/T$ is given in Figure 3c. The value of heat of adsorption was determined from the slope $\left(\frac{-\Delta Q_{ads}}{2.303RT}\right)$ of the graph. The value of heat of adsorption is given in Table 4. It is evident from the Table 2 that (ΔQ_{ads}) has negative value which indicates that inhibitor adsorption decreases with increase in the temperature hence decrease in inhibitor efficiency. The negative value of (ΔQ_{ads}) also suggested that the adsorption of inhibitor is an exothermic process [26].

Table 2. Thermodynamic parameters for mild steel in 1 M HCl in absence and presence of Glutamine

Inhibitor conc. (ppm)	E_a (kJmol^{-1})	ΔH^* (kJmol^{-1})	ΔQ_{ads} (kJmol^{-1})
Blank	38.1	35.4	-
100	74.0	69.34	-19.7

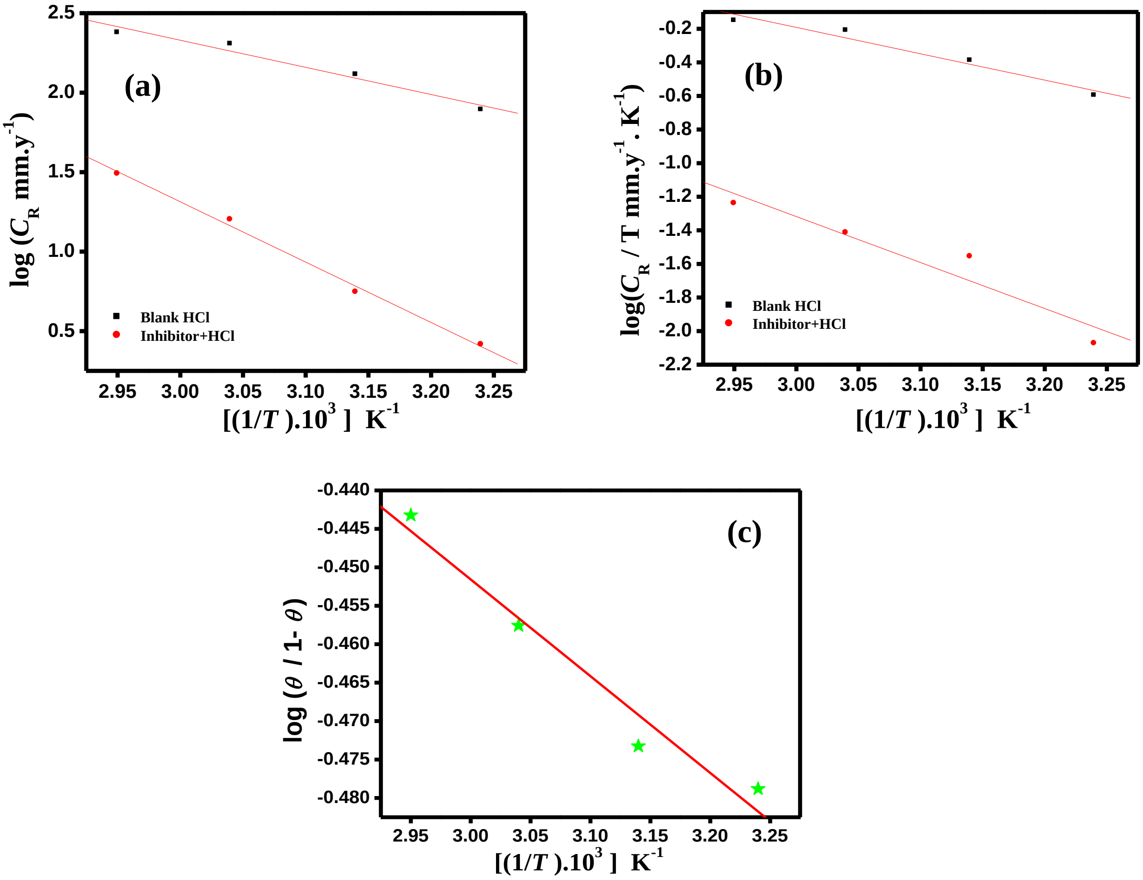

Figure 3. (a) Arrhenius plot of log C_R vs. 1000/T (b) Transition state plot of log C_R/T vs. 1000/T (c) $Log\left(\frac{\theta}{1-\theta}\right)$ versus 1/T for mild steel in 1 M HCl in the absence and the presence Glutamine.

The standard free energy of adsorption, $\Delta G°_{ads}$ and the values of equilibrium constant, K_{ads} at different temperatures were calculated from the equation;

$$K = \frac{\theta}{C(1-\theta)} \tag{7}$$

$$\Delta G^{\circ}_{ads} = -RT\ln(55.5K_{ads}) \tag{8}$$

The value 55.5 in the above equation is the concentration of water in solution in mol/lit. The values of ΔG_{ads} are given in Table 3.

The negative values of ΔG_{ads} indicate the spontaneity of the adsorption of inhibitor molecules on the metal surface. Generally, the values of ΔG_{ads} up to -20 KJ mol^{-1} are consistent with the electrostatic interaction (physisorption) of charged molecules and the charged metal, while those around -40 KJ mol^{-1} or more negative are associated with sharing or transfer of electrons from inhibitor molecules to the metal surface forming coordinate type bond (chemisorption) [27]. The calculated values of ΔG_{ads} obtained range from -38.0 to -40.2 KJ mol^{-1}, indicating that the adsorption of the inhibitor on mild steel surface is by chemical adsorption [28].

Table 3. Standard free energy of adsorption of mild steel in 1 M HCl in absence and presence of Glutamine at different temperatures

Temperature (K)	-ΔG_{ads} (kJ mol^{-1})
308	38.0
318	39.3
328	40.0
338	40.2

3.2.1. Adsorption isotherm

The adsorption isotherm provides useful information for the mechanism of corrosion inhibition. The surface coverage, θ, was calculated from the equation,

$$\theta = \frac{C_{\mathrm{R}} - {}^{\mathrm{inh}}C_{\mathrm{R}}}{C_{\mathrm{R}}} \qquad (9)$$

where, C_{R} and ${}^{\mathrm{inh}}C_{\mathrm{R}}$ are the corrosion rates of mild steel in the absence and presence of Glutamine respectively. By fitting the θ values obtained from weight loss data to various isotherms namely Langmuir, Temkin, and Frumkin, the best fit was obtained with the Langmuir isotherm [29]. A straight line was obtained on plotting (C/θ) vs θ for Langmuir isotherm with regression coefficient (R^2= 0.99971) confirm this approach as shown in Figure 4.

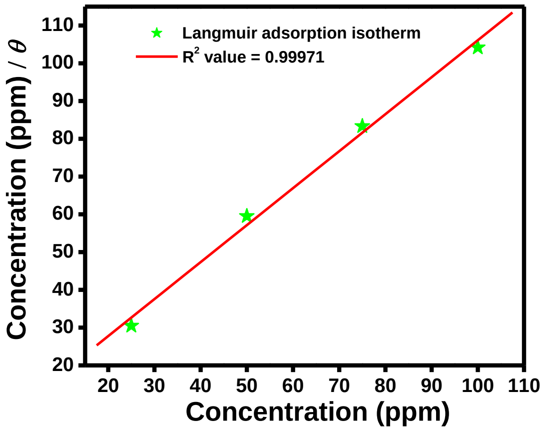

Figure 4. The Langmuir adsorption isotherm plots for mild steel at different concentrations of Glutamine by weight loss method.

3.3. Quantum Chemical Calculations

The structure and electronic parameters were obtained by means of theoretical calculations using the computational methodologies of quantum chemistry. The optimized molecular structures and frontier molecular orbital density distribution of the studied molecule are shown in Figure 5. The calculated quantum chemical parameters such as E_{HOMO}, E_{LUMO}, $\Delta E_{\mathrm{LUMO\text{-}HOMO}}$, dipole moments ($\mu$) are listed in Table 4. The molecular structure of Glutamine shows that the molecules seems to adsorb on mild steel surface by sharing of electrons of the nitrogen atoms with iron to form coordinated bonds and π-electron interactions of the aromatic rings.

Table 4. Calculated quantum chemical parameters of Glutamine.

Quantum Parameters	Glutamine
HOMO (hartree)	-0.22765
LUMO (hartree)	0.03398
ΔELUMO-HOMO (hartree)	0.26163
Dipole Moment (μ)	3.2845

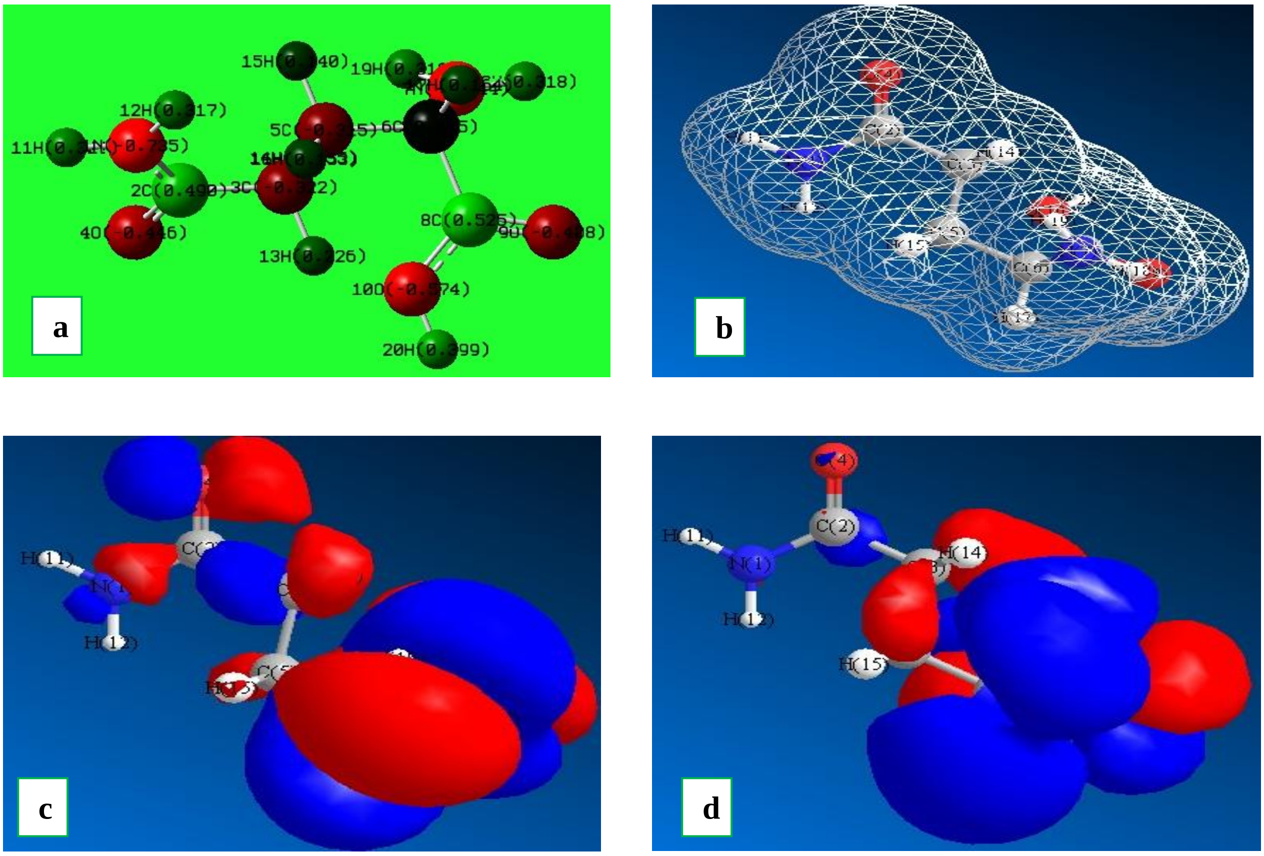

Figure 5. (a) Optimized molecular structure (b) total charge density (c) HOMO and (d) LUMO molecular orbital density distribution of Glutamine.

The value of highest occupied molecular orbital, E_{HOMO} indicates the tendency of the molecule to donate electrons to acceptor molecule with empty and low energy orbital. Therefore, the energy of the lowest unoccupied molecular orbital, E_{LUMO} indicates the tendency of the molecule to accept electrons [30]. The energy gap Δ*E* is an important parameter which is related to reactivity of the inhibitor molecule towards the metal surface. The interaction of inhibitor molecule to the metal surface is related to transfer of electrons from inhibitor to metal surface [31].

3.4. Mechanism of adsorption and inhibition

The data obtained from the different methods conclude that the inhibition by Glutamine might due to adsorption at the metal/solution interface. The essential effect of Glutamine used as corrosion inhibitor is due to the presence of free electron pairs in the oxygen and the nitrogen atoms, π-electrons on the aromatic rings, molecular size, and mode of interaction with the metal surface and the formation of metallic complexes. The unshared and π-electrons interact with d-orbital of Fe to provide a protective film. The inhibitive properties of such compounds depend on the electron densities around the active centre; the inhibition mechanism of the inhibitor is a combination of surface blockage and electrostatic repulsion between adsorbed surfactant layer and chloride ions [32]. The adsorption density of inhibitor depends on the inhibitor concentration. The inhibition of these reactions would obviously depend on the degree of the surface coverage of the metal with the adsorbate. Adsorption is assumed to occur on the surface of the metal between the aggressive Cl^- and the inhibitor molecules, on the other. The order of the increasing inhibition, the molecular size of the inhibitor and consequently the number of adsorption centres plays an important role in the enhancement of the protection of carbon steel against corrosion [33].

4. CONCLUSIONS

1. Glutamine is good inhibitor for mild steel in 1 M HCl. The inhibition efficiency increased with increasing the concentration of the inhibitor up to a maximum of 96% at 100 ppm.

2. The adsorption of inhibitor molecules on the mild steel surface in 1 M HCl solution followed Langmuir adsorption isotherm.

3. The negative values of ΔG_{ads} showed the spontaneity of the adsorption.

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