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# L-Tryptophan as green corrosion inhibitor for low carbon steel in hydrochloric acid solution

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**Abstract** The inhibition behavior of low carbon steel in 1 M HCl by L-tryptophan was investigated with weight loss experiment and Tafel polarization curve in the used temperature range (298–328 K). All the experimental results show that L-tryptophan has excellent corrosion inhibition performance and the most effective concentration of inhibitor is $1 \times 10^{-2}$ mol $L^{-1}$. The Tafel polarization curve results indicate that L-tryptophan acts more as a cathodic than anodic inhibitor. The adsorption of L-tryptophan on the surface of low carbon steel obeys the Langmuir adsorption isotherm, and the thermodynamic parameters were determined and discussed. The adsorption behavior of L-tryptophan at Fe surface (1 1 0) was also investigated by the molecule dynamics simulation method and density functional theory. The results indicated that the L-tryptophan could adsorb firmly on the Fe surface through the indole ring with $\pi$-electrons and nitrogen/oxygen atom with lone-pair electrons in its molecule.

## Introduction

Corrosion inhibitors have long been used for daily operation of recirculating cooling water system, industrial acid cleaning, oil well acidification, and descaling due to their economical and efficient properties [1–3]. However, the environmental risk of these inhibitors has been assessed in the recent decades due to their toxic effects on aquatic organisms and plants. The application of the traditional inhibitors, such as chromate, nitrite, polyphosphate, and organic phosphonate has been prohibited or limited in many countries [4, 5]. As a result, the current research trend for corrosion inhibitors is toward more environmental-friendly green chemicals [6].

Amino acids are nontoxic, relatively cheap, and easy to produce with purities greater than 99%. Recently, with respect to amino acid as corrosion inhibitor, many achievements have been gained in laboratory studies [7–12]. Furthermore, as environmental and non-phosphorus corrosion and scale inhibitors, poly (aspartic acid) and poly (epoxy succinic acid), which are the amino acid derivatives, have been widely used in industrial recirculating cooling water systems, showing an excellent performances [13, 14].

L-Tryptophan is a derivative of indole. Based on the analysis of molecule structure of L-tryptophan (see Fig. 1), it has the potential to become an excellent corrosion inhibitor. Moretti and Guidi [15] reported the tryptophan was effective in inhibiting copper corrosion in aerated 0.5 M sulfuric acid in the 20–50 °C temperature range, and the corrosion rate did not rise dramatically as temperature increased. Ashassi-Sorkhabi et al. [16] reported that compared with the other amino acids, including alanine, leucine, valine, proline, and methionine, tryptophan exhibited the best inhibition efficiency toward the corrosion of aluminum in 1 M HCl + 1 M $H_2SO_4$, which was attributed to the excess nitrogen atoms in molecule structure and the relatively large molecule volume. However, the recent research about the inhibition effect of L-tryptophan on low carbon steel in corrosive medium is rare. In this study, the inhibition efficiency of L-Tryptophan was evaluated by weight loss experiments under different temperature. Then, the polarization technique was used to estimate the effect of the L-tryptophan on cathodic and anodic reactions. In

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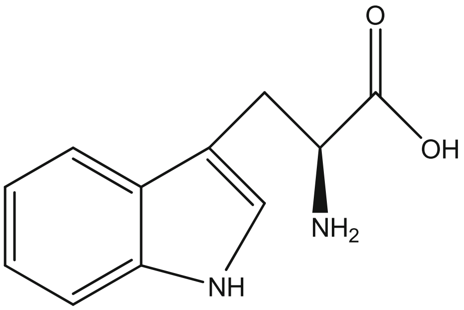

**Fig. 1** Molecule structure of L-tryptophan

addition, in order to deeply understand the interactions between L-tryptophan and Fe surface (1 1 0), quantum chemistry (DFT) was employed to discuss the charge distribution and frontier orbital energy and molecule simulation study were performed to simulate the adsorption of L-tryptophan on Fe surface (1 1 0).

## Materials and methods

### Materials

L-Tryptophan was purchased from Acros Company (its molecule formula is shown in Fig. 1). The concentration range of L-tryptophan used was $1 \times 10^{-5}$–$1 \times 10^{-2}$ mol $L^{-1}$. The corrosive medium tested in this experiment was a 1 M HCl, which was widely used in many fields of industrial applications. The 1 M HCl corrosive solution was made with AR grade HCl and double distilled water.

The composition of the low carbon steel sample was (wt%): 0.18C, 0.30Mn, 0.15Si, 0.02S, 0.02P, the balance being Fe. The working electrode (WE) was in the form of a rod machined into a cylindrical form embedded in epoxy resin leaving an open surface area of 0.75 $cm^2$. Prior to the polarization measurements, the exposed surface was pretreated by using emery paper grade (320, 600, 800, 1,200, and 1,500) and then rinsed by double distilled water, degreased with acetone, and then dried at room temperature before use.

### Weight loss method

Low carbon steel coupons of dimension 2.5 × 2.0 × 2.0 $cm^3$ were used for weight loss measurements. The polished and pre-weighted specimens were suspended in 500 ml 1 M HCl solutions with and without L-tryptophan at different concentration and allowed to stand for 3 h in the used temperature range. The HCl solutions were deaerated with ultrapure nitrogen bubbling. Afterward, the specimens were rinsed with water, cleaned with acetone, dried, and weighted. Duplicate tests were conducted for each experiment. The corrosion rate ($W_{corr}$) and the percentage of inhibition efficiency ($IE_W$, %) over the exposure period were calculated using the following equations:

$$W_{corr} = \frac{m_1 - m_2}{At}$$

where $m_1$ and $m_2$ are the weight loses (mg) before and after immersion in the test solution, $A$ the area of the specimens ($cm^2$), and $t$ the exposure time (h).

$$IE_W(\%) = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100,$$

where $W_{corr}$ and $W'_{corr}$ are the uninhibited and inhibited corrosion rate (in terms of mg $cm^{-2}$ $h^{-1}$), respectively.

### Electrochemical studies

The electrochemical measurements were performed in a conventional three-electrode assembly with specimens as WE, a platinum foil of 2.0 cm × 1.0 cm as counter electrode, and a saturated calomel electrode (SCE) provided with a Luggin capillary as reference electrode, connected to a potentiostat (Princeton, Parstat 2273) and a PC computer. The WE was placed vertically facing the counter electrode, and a reference electrode was placed near the WE. The WE was immersed in 1 M HCl solution for 30 min until a steady-state open circuit potential (OCP) was obtained. The HCL solution was degassed with ultrapure nitrogen bubbling for 30 min to avoid any reactions with dissolved oxygen. Tafel polarization scans were carried out by changing the electrode potential automatically from −250 to +250 mV versus OCP with a scan rate of 0.166 mV/s. The experiment data recordings and the calculation of the electrochemical parameters were performed using PowerSuite2.58 Princeton software.

### Theoretical studies

The quantum chemical calculations were carried out with Gaussian03W at density functional theory (DFT) level by B3LYP method, using 6-311*G(d,p) basis set. This basis set provided accurate geometry and electronic properties for a wide range of organic compounds [17].

The molecule dynamics simulation was performed using the software, Material Studio 4.2. The surface of Fe (1 1 0) was chosen to simulate the adsorption process. The MD calculation of the simulation of the interaction between the L-Tryptophan dissolved in $H_2O$ and the Fe (1 1 0) surface was carried out in a simulation box (32 Å × 32 Å × 60 Å) with periodic boundary conditions in order to simulate a representative part of an interface devoid of any arbitrary boundary effects. L-Tryptophan molecule was energy optimized, Fe (1 1 0) surface and water layers was constructed using the amorphous cell module. The molecule dynamics simulation was performed under 298 K, NVT ensemble, with a time step of 0.1 fs and simulation time of 50 ps. Details of simulation process can be referred to some previous literatures [18, 19].

The interaction energy $E_{\text{Fe-inhibitor}}$ of Fe surface with the L-tryptophan was calculated according to the following equation:

$$E_{\text{Fe}-\text{inhibitor}} = E_{\text{complex}} - (E_{\text{Fe}} + E_{\text{inhibitor}})$$

where $E_{\text{complex}}$ is the total energy of the Fe crystal together with the adsorbed inhibitor molecule, $E_{\text{Fe}}$ and $\text{E}_{\text{inhibitor}}$ the total energy of the iron crystal and free inhibitor molecule, respectively.

## Results and discussion

### Weight loss measurements

The weight loss method is widely used in laboratory and factory due to its simple equipment and accurate data of average corrosion. Table 1 shows the corrosion rate and inhibition efficiency of low carbon steel by weight loss measurements at different concentrations of L-tryptophan in 1 M HCl under various temperatures. Data in Table 1 indicate that the corrosion rate depends on two factors: inhibitor concentration and temperature. It is clearly seen that the corrosion rates are reduced in the presence of L-tryptophan compared to its absence for low carbon steel in 1 M HCl. The inhibiting behaviors can be attributed to the adsorption of inhibitor on the surface of low carbon steel. The corrosion rate of low carbon steel decreases, whereas the inhibition efficiency increases with increasing inhibitor concentration at all temperatures. Increased inhibition efficiency with concentration indicates that more L-tryptophan molecules are adsorbed on the low carbon steel surface at high concentration, leading to form the protective film [20]. Also the inhibition efficiencies are observed to decrease with increasing temperature both in the absence and presence of inhibitors. This is mainly because that the adsorbed film is unstable and easily damaged at high temperature [21]. The highest inhibition efficiency of 90.8% was obtained for L-tryptophan for a concentration of $1 \times 10^{-2}$ mol $\text{L}^{-1}$ at 298 K.

### Polarization measurements

The anodic and cathodic polarization curves for the corrosion of low carbon steel in 1 M HCl with different concentrations of L-tryptophan at 298–338 K are shown in Figs. 2, 3, 4, 5. The values of corrosion current density ($j_{\text{corr}}$), the corrosion potential ($E_{\text{corr}}$), the cathodic Tafel slopes ($b_{\text{c}}$), the anodic Tafel slopes ($b_{\text{a}}$), and the inhibition efficiency ($\text{IE}_{\text{I}}$) as function of L-tryptophan concentrations at temperatures between 298 and 338 K are given in Table 2. The $j_{\text{corr}}$ values were used to calculate the inhibition efficiency, $IE_{\text{I}}$ (%), using the following equation:

$$\text{IE}_{\text{I}}(\%) = \frac{j^0_{\text{corr}} - j_{\text{corr}}}{j^0_{\text{corr}}} \times 100$$

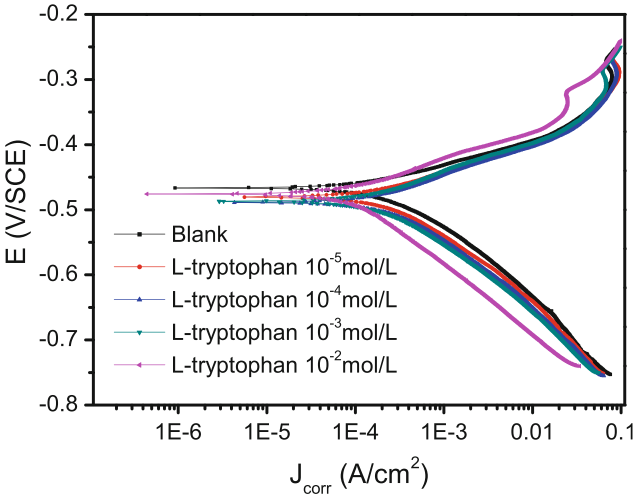

**Fig. 2** Tafel polarization curves for low carbon steel in 1 M HCl solution containing various concentration of L-tryptophan at 298 K

**Table 1** Inhibition efficiency for different concentration of L-tryptophan for the corrosion of low carbon steel in 1 M HCl obtained from weight loss measurement

| Inhibitor concentration (mol/L) | Corrosion rate (mg $\text{cm}^{-2}$ $\text{h}^{-1}$) | | | | $\text{IE}_{\text{W}}$ (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | 298 K | 308 K | 318 K | 328 K | 298 K | 308 K | 318 K | 328 K |
| Blank | 3.72 | 10.9 | 37.8 | 87.4 | – | – | – | – |
| $1 \times 10^{-5}$ | 2.06 | 6.79 | 24.9 | 65.9 | 44.5 | 37.7 | 33.9 | 24.5 |
| $1 \times 10^{-4}$ | 1.12 | 3.99 | 18.3 | 48.7 | 69.8 | 63.4 | 51.5 | 44.2 |
| $1 \times 10^{-3}$ | 0.48 | 2.84 | 11.9 | 40.3 | 86.9 | 73.9 | 68.4 | 53.9 |
| $1 \times 10^{-2}$ | 0.34 | 1.34 | 7.48 | 27.3 | 90.8 | 87.7 | 80.2 | 68.7 |

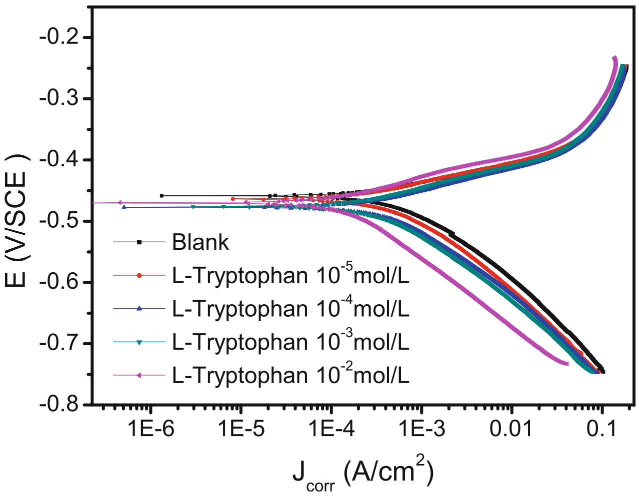

**Fig. 3** Tafel polarization curves for low carbon steel in 1 M HCl solution containing various concentration of L-tryptophan at 308 K

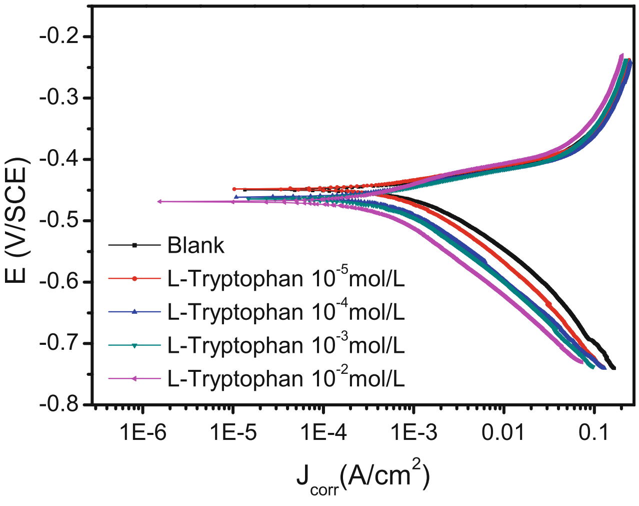

**Fig. 4** Tafel polarization curves for low carbon steel in 1 M HCl solution containing various concentration of L-tryptophan at 318 K

where $j^0_{corr}$ and $j_{corr}$ are the corrosion current density values in the absence and presence of L-tryptophan, respectively.

The addition of L-tryptophan decreases the corrosion current density ($j_{corr}$) values continuously with increasing inhibitor concentration at all temperature. The data also show that the $j_{corr}$ increases, whereas the $IE_I$ decreases considerable as rising temperature. The maximum inhibition efficiency ($IE_I$), 92.7%, was obtained in L-tryptophan at the highest concentration of $1 \times 10^{-2}$ mol $L^{-1}$ and at the lowest temperature of 298 K. The changing trends of $j_{corr}$ and $IE_I$ reflect two facts: one is when the adsorption–desorption process reached equilibrium under a certain temperature, a higher coverage of inhibitor on the surface is obtained in a solution with highest concentrations of inhibitor. The other is that an increase in temperature results in the desorption of originally adsorbed L-tryptophan molecule from the metal surface, which is consistent with the result of weight loss measurements.

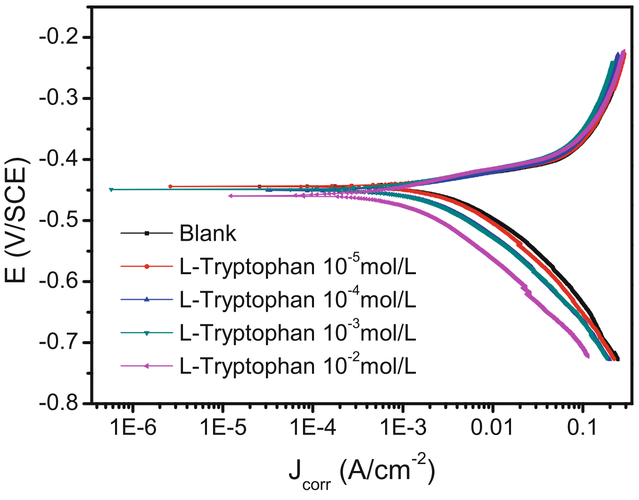

**Fig. 5** Tafel polarization curves for low carbon steel in 1 M HCl solution containing various concentration of L-tryptophan at 328 K

Figures 2, 3, 4, 5 shows the polarization profiles for low carbon steel in 1 M HCl in the absence and presence of L-tryptophan at various used temperatures. In the cathodic domain, it is clear that the cathodic current density decreases with increasing the concentration of the inhibitor, indicating the inhibition of the hydrogen evolution reaction. In addition, the parallel cathodic Tafel curves show that the hydrogen evolution is activation controlled and the reduction mechanism is not affected by the presence of the L-tryptophan [22, 23]. The unchanged cathodic Tafel slopes also show that the inhibiting action of L-tryptophan is simply blocking of the active site of the metal surface. In the anodic domain, it seems that L-tryptophan has no obvious effect on the current density at low concentration under investigated temperature range, and even in some cases, the acceleration of anodic reactions is observed. But, the addition of $1 \times 10^{-2}$ mol $L^{-1}$ L-tryptophan markedly shifts the anodic curves toward lower current densities especially at 298 K, indicating a strong inhibition effect of the anodic reaction. The addition of L-tryptophan shifts the corrosion potential ($E_{corr}$) in the negative direction compared to the blank in 1 M HCl, suggesting that L-tryptophan acts more as a cathodic than anodic inhibitor.

## Effect of temperature

In order to examine the effect of temperature on the corrosion process and elucidate the mechanism of inhibition, the Arrhenius equation is used here:

$$\ln j_{corr} = \frac{-E_a}{2.303RT} + \log A$$

**Table 2** Corrosion parameters of low carbon steel in 1 M HCl in presence of L-tryptophan as an inhibitor

| Inhibitor concentration (mol $L^{-1}$) | $j_{corr}$ (μA $cm^{-2}$) | $E_{corr}$ (mV) vs. SCE | $b_a$ (mV $dec^{-1}$) | $-b_c$ (mV $dec^{-1}$) | Inhibition efficiency $IE_I$ (%) |
|---|---|---|---|---|---|
| 298 K | 269 | −466 | 47 | 93 | – |
| $1 \times 10^{-5}$ | 136 | −480 | 50 | 96 | 49.4 |
| $1 \times 10^{-4}$ | 85 | −489 | 57 | 99 | 68.4 |
| $1 \times 10^{-3}$ | 55 | −487 | 55 | 97 | 79.2 |
| $1 \times 10^{-2}$ | 19 | −475 | 49 | 104 | 92.7 |
| 308 K | 493 | −458 | 43 | 112 | – |
| $1 \times 10^{-5}$ | 276 | −463 | 44 | 109 | 43.9 |
| $1 \times 10^{-4}$ | 170 | −477 | 47 | 106 | 65.5 |
| $1 \times 10^{-3}$ | 132 | −476 | 47 | 103 | 73.2 |
| $1 \times 10^{-2}$ | 64 | −470 | 43 | 108 | 86.9 |
| 318 K | 1691 | −457 | 41 | 114 | – |
| $1 \times 10^{-5}$ | 1057 | −448 | 38 | 121 | 37.5 |
| $1 \times 10^{-4}$ | 926 | −461 | 37 | 109 | 45.2 |
| $1 \times 10^{-3}$ | 772 | −464 | 38 | 110 | 54.3 |
| $1 \times 10^{-2}$ | 424 | −468 | 49 | 108 | 74.9 |
| 328 K | 5256 | −444 | 44 | 125 | – |
| $1 \times 10^{-5}$ | 4026 | −443 | 40 | 119 | 23.4 |
| $1 \times 10^{-4}$ | 2980 | −450 | 40 | 114 | 43.3 |
| $1 \times 10^{-3}$ | 2749 | −448 | 40 | 114 | 47.7 |
| $1 \times 10^{-2}$ | 1718 | −459 | 49 | 121 | 67.3 |

where $E_a$ represents the apparent activation energy, $R$ the gas constant, $T$ the absolute temperature, $A$ the pre-exponential factor, and $j_{corr}$ the corrosion rate.

Arrhenius plots for the corrosion density of low carbon steel in the absence and presence of L-tryptophan in 1 M HCl are shown in Fig. 6. Values of apparent activation energy are determined from the slope of ln ($j_{corr}$) versus $1/T$ plots and tabulated in Table 3. It is observed that the apparent activation energy ($E_a$) is higher in the presence of the inhibitor than in blank acid solution, and it increases with increasing the inhibitor concentration. The values for $E_a$ in 1 M HCl in the absence and presence of $1 \times 10^{-2}$ mol $L^{-1}$ L-tryptophan are 82.15 and 124.1 kJ $mol^{-1}$, respectively. As described in previous literature, the higher activation energy value of corrosion process in the presence of inhibitor when compared to that in its absence is attributed to the physisorption of inhibitor [6]. The energy barrier of corrosion process increases with the inhibitor concentration indicating that the physisorption create an adsorptive film to retard the charge and mass transfer process.

**Table 3** Activation parameters of low carbon steel in 1 M HCl with and without L-tryptophan

| Inhibitor concentration (mol $L^{-1}$) | $E_a$ (kJ $mol^{-1}$) |
|---|---|
| Blank | 82.15 |
| $1 \times 10^{-5}$ | 93.08 |
| $1 \times 10^{-4}$ | 100.2 |
| $1 \times 10^{-3}$ | 109.1 |
| $1 \times 10^{-2}$ | 124.1 |

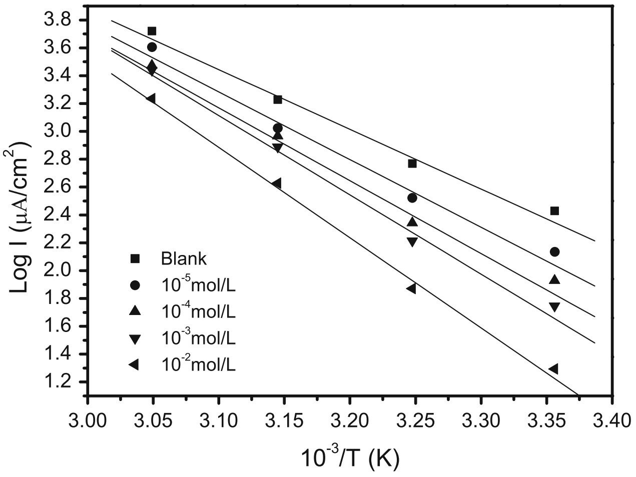

**Fig. 6** Arrhenius plot for low carbon steel corrosion in 1 MHCl in the absence and presence of various concentrations of L-tryptophan

## Adsorption isotherm

Basic information on the interaction between the inhibitor and the low carbon steel surface can be provided by the adsorption isotherm. The value of surface coverage ($\theta$) has been obtained from polarization measurements for various concentrations of L-tryptophan. Here $\theta$ can be written as: $\theta = \mathrm{IE_I}(\%)/100$.

The values of $\theta$ were fitted to different isotherms, and the Langmuir isotherm was found to be the best description of the adsorption behavior of the L-tryptophan. Langmuir isotherm can be written as:

$$\frac{C}{\theta} = \frac{1}{K_{\mathrm{ads}}} + C,$$

where $K_{\mathrm{ads}}$ is the constant of adsorption. The relationship between $C/\theta$ and $C$ at 298, 308, 318, and 328 K is shown in Fig. 7.

The plot of $C/\theta$ versus inhibitor concentration ($C$) showed a linear correlation of slope close to unity, suggesting that the adsorption of L-tryptophan on iron surface interface obeys Langmuir adsorption isotherm. The constant $K_{\mathrm{ads}}$ may be determined from the intercept in Fig. 7. The value of $K_{\mathrm{ads}}$ is related to the standard free energy of adsorption, $\Delta G^0_{\mathrm{ads}}$ by the following equation:

$$K_{\mathrm{ads}} = \frac{1}{55.5}\exp\left(\frac{-\Delta G^0_{\mathrm{ads}}}{RT}\right),$$

where $R$ is the gas constant and $T$ the absolute temperature. The value of 55.5 is the concentration of water in solution expressed in mol $\mathrm{dm}^{-3}$. The equilibrium constant and standard free energy for low carbon steel in 1 M HCl in the presence of L-tryptophan are given in Table 4. Generally speaking, the negative value of $\Delta G^0_{\mathrm{ads}}$ means that the adsorption of L-tryptophan on the low carbon steel is spontaneous. It is well known that values of $\Delta G^0_{\mathrm{ads}}$ around $-20$ kJ $\mathrm{mol}^{-1}$ or lower indicate a physisorption. The adsorption process is caused by electrostatic attraction between charged metal surface and charged organic molecules. Values around $-40$ kJ $\mathrm{mol}^{-1}$ or higher are regarded as chemisorptions. However, the judgment of the adsorption type with value of $\Delta G^0_{\mathrm{ads}}$ between $-20$ and $-40$ kJ $\mathrm{mol}^{-1}$ remains dispute [24–27]. It is found that the $\Delta G^0_{\mathrm{ads}}$ values for L-tryptophan are almost $-33$ kJ $\mathrm{mol}^{-1}$. So it could be inferred that adsorption may involve physisorption and chemisorption.

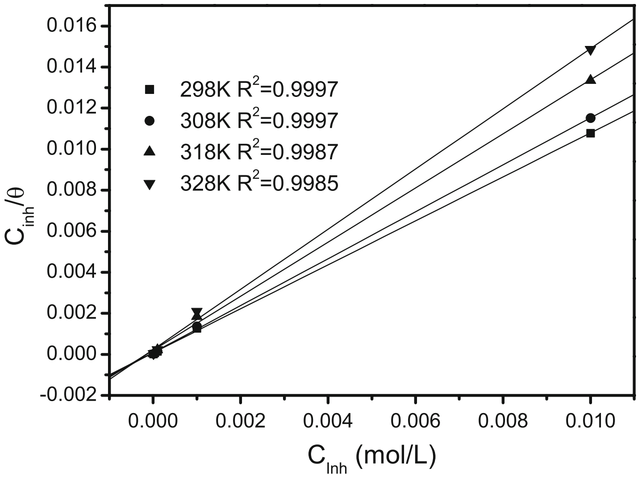

**Fig. 7** Langmuir adsorption isotherm plot for the adsorption of L-tryptophan on the surface of low carbon steel in 1M HCl at various temperatures

**Table 4** Thermodynamic parameters for low carbon steel in 1 M HCl in the presence of L-Tryptophan at different temperatures

| Inhibitors | Temperature (K) | $K_{\mathrm{ads}}$ | $-\Delta G^0_{\mathrm{ads}}$ (KJ $\mathrm{mol}^{-1}$) |
|---|---|---|---|
| L-Tryptophan | 298 | 13154 | 33.4 |
| | 308 | 11584 | 34.2 |
| | 318 | 5047 | 33.1 |
| | 328 | 4259 | 33.7 |

For easily protonated L-tryptophan, there are two ways to adsorption. First, it may be adsorbed via donor–acceptor interactions between the $\pi$-electrons of the indole rings and the unshared electrons pairs of the heteroatoms to form a bond with the vacant d orbitals of the metal surface [28]. Second, in acidic media, $-\mathrm{NH_2}$ of amino is readily protonated, which might adsorb onto the metallic surface via the negatively charge acid anions (e.g., $\mathrm{Cl}^-$, $\mathrm{SO_4}^{2-}$) [29]. Physical adsorption and chemical adsorption will lead to the formation of a protective film.

## Computational study

In the past few decades, quantum chemistry has become an effective way to study the correlation of the molecule structure and inhibition performance [17, 30]. The optimized molecule structure, the highest occupied molecule orbitals, the lowest unoccupied molecule orbital and the charge distribution of L-tryptophan molecule using DFT functional (B3LYP/6-311*G) are shown in Fig. 8, and the calculated quantum chemical indices $E_{\mathrm{HOMO}}$, $E_{\mathrm{LUMO}}$, $\Delta E$, and dipole moment (μ) are given in Table 5.

Figure 8 shows that in L-tryptophan molecule, C5, C12, C13, C14, C15, N7, N10, O2, and O4 carry more negative charges, while C8 and C6 carry more positive charges. This means that C5, C12, C13, C14, C15, N7, N10, O2, and O4 are the negative charge centers, which can offer electrons to the Fe atoms to form coordinate bond, and C8 and C6 are the positive charge centers, which can accept electrons from orbital of Fe atoms to form feedback bond. The optimized structure is in accordance with the fact that excellent corrosion inhibitors can not only offer electrons to unoccupied orbital of the metal, but also accept free

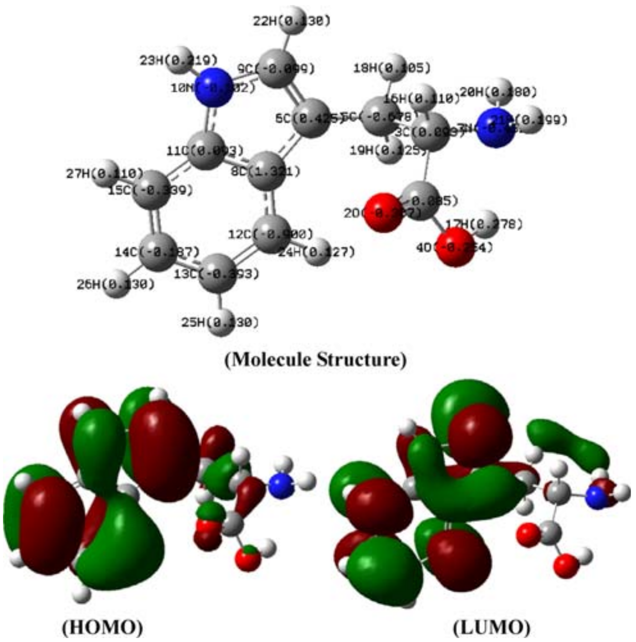

**Fig. 8** The optimized molecule structure, molecule orbital plots, and the charge density distribution of L-tryptophan

**Table 5** Quantum chemical indices for L-tryptophan

| Calculated parameters for tryptophan | Value |
|---|---|
| $E_{\mathrm{HOMO}}$ (eV) | −5.687 |
| $E_{\mathrm{LUMO}}$ (eV) | −0.6258 |
| $\Delta E$ ($E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) (eV) | 5.0612 |
| $-E_{\mathrm{total}}$ (eV) | 18634.3 |
| Dipole moment ($D$) | 5.6402 |

electrons from the metal. Therefore, it can be inferred that indole ring, nitrogen, and oxygen atoms are the possible active adsorption sites.

According to the description of frontier orbital theory, HOMO is often associated with the electron donating ability of an inhibitor molecule. High $E_{\mathrm{HOMO}}$ values indicate that the molecule has a tendency to donate electrons to the metal with unoccupied molecule orbitals. $E_{\mathrm{LUMO}}$ indicates the ability of the molecules to accept electrons. The lower value of $E_{\mathrm{LUMO}}$ is, the easier acceptance of electrons from metal surface. The gap between the LUMO and HOMO energy levels of the inhibitor molecules is another important index, the low absolute values of the energy band gap ($\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) means good inhibition efficiency. The data listed in Table 5 verified that L-tryptophan has high value of $E_{\mathrm{HOMO}}$ and low value of $E_{\mathrm{LUMO}}$ with low energy band gap.

In order to get more information on the adsorption behavior, molecule dynamics simulation studies were performed to simulate the adsorption structure of the L-tryptophan molecule on low carbon steel surface in presence of water molecules and further analyze the interactions between L-tryptophan molecule and Fe (1 1 0) surface.

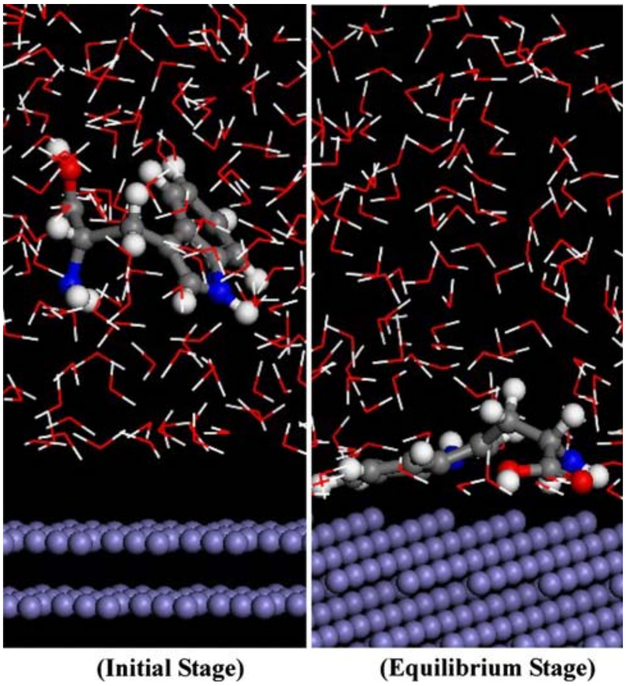
(Initial Stage) (Equilibrium Stage)

**Fig. 9** L-Tryptophan adsorbed on Fe surface in water solution

Figure 9 shows the initial and equilibrium configuration of L-tryptophan in water solution. It can be easily seen from Fig. 9 that L-tryptophan molecule moves to the iron surface, and the minimum distance between the L-tryptophan molecule and Fe surface is 2.12 Å. When the adsorption process reaches a balance, all the atoms are almost in the same plane, and the L-tryptophan molecule is nearly parallel to the Fe (1 1 0) surface. By comparing the two different configurations, it is concluded that the L-tryptophan can be absorbed on the Fe (1 1 0) surface through the indole ring and nitrogen/oxygen atoms. A number of lone pairs electrons on atoms like N and O as well as $\pi$-electron clouds on the indole ring contribute a great deal to the adsorption process. This planar adsorption configuration increases the contact area and prevents the water molecule from penetrating into the Fe surface. Adsorption energy calculated for the adsorption of L-tryptophan on Fe surface in the presence of water molecules equals −29.5 kJ mol$^{-1}$, which implies that the interaction between L-tryptophan molecule and Fe surface is strong [31, 32].

## Conclusions

In this research, chemical and electrochemical measurements were used to study the corrosion inhibition of low carbon steel in 1 M HCl using L-tryptophan as corrosion inhibitors. The principle conclusions can be summarized as follows.

1. L-Tryptophan was found to be effective inhibitors for low carbon steel corrosion in 1 M HCl, especially at the concentration of $1 \times 10^{-2}$ mol $L^{-1}$.
2. Tafel polarization measurements showed that L-Tryptophan acts as cathodic-type inhibitor.
3. The data obtained from electrochemical measurements fit well the Langmuir adsorption isotherm, and the thermodynamic parameters obtained indicated that the adsorption of L-tryptophan onto the low carbon steel surface may involve physisorption and chemisorption.
4. The quantum calculation determined the possible adsorption centers of L-tryptophan. Molecule dynamics simulation results showed that L-tryptophan molecules assumed a nearly flat orientation with respect to the Fe (1 1 0) surface. The calculated adsorption energy between a L-tryptophan molecule and Fe surface is $-29.5$ kJ $mol^{-1}$.

## References

1. Demadis KD, Mavredaki E, Stathoulopoulou A, Neofotistou E, Mantzaridis C (2007) Desalination 213:38
2. Behpour M, Ghoreishi SM, Gandomi-Niasar A, Soltani N, Salavati-Niasari M (2009) J Mater Sci 44(10):2444. doi:10.1007/s10853-009-3309-y
3. El-Meligi AA, Turgoose S, Ismail AA, Sanad SH (2000) Br Corros J 35(1):75
4. Choi DJ, You SJ, Kim JG (2002) Mater Sci Eng A 335(1–2):228
5. Ketsetzi A, Stathoulopoulou A, Demadis KD (2008) Desalination 223(1–3):487
6. Umoren SA, Obot IB, Obi-Egbedi NO (2009) J Mater Sci 44(1):274. doi:10.1007/s10853-008-3045-8
7. Badawy WA, Ismail KM, Fathi AM (2006) Electrochim Acta 51(20):4182
8. Morad MS (2008) J Appl Electrochem 38(11):1509
9. Olivares O, Likhanova NV, Gómez B, Navarrete J, Llanos-Serrano ME, Arce E, Hallen JM (2006) Appl Surf Sci 252(8):2894
10. Olivares-Xometl O, Likhanova NV, Domínguez-Aguilar MA, Arce E, Dorantes H, Arellanes-Lozada P (2008) Mater Chem Phys 110(2–3):344
11. Barouni K, Bazzi L, Salghi R, Mihit M, Hammouti B, Albourine A, El Issami S (2008) Mater Lett 62(19):3325
12. Ismail KM (2007) Electrochim Acta 52(28):7811
13. Liu GH, Xi DL, Li Y, Lu Z (2003) Corros Prot 24(11):480
14. Silverman DC, Kalota DJ, Stover FS (1995) Corrosion 51(11):818
15. Moretti G, Guidi F (2002) Corros Sci 44(9):1995
16. Ashassi-Sorkhabi H, Ghasemi Z, Seifzadeh D (2005) Appl Surf Sci 249(1–4):408
17. Gece G (2008) Corros Sci 50(11):2981
18. Khaled KF, Fadl-Allah SA, Hammouti B (2009) Mater Chem Phys 117(1):148
19. Khaled KF (2009) Electrochim Acta 54(18):4345
20. Rao VS, Singhal LK (2009) J Mater Sci 44(9):2327. doi:10.1007/s10853-008-2976-4
21. Shukla SK, Quraishi MA (2009) Corros Sci. doi: 10.1016/j.corsci.2009.05.020
22. Aljourani J, Raeissi K, Golozar MA (2009) Corros Sci 51(8):1836
23. Prabhu RA, Venkatesha TV, Shanbhag AV, Kulkarni GM, Kalkhambkar RG (2008) Corros Sci 50(12):3356
24. de Souza FS, Spinelli A (2009) Corros Sci 51(3):642
25. Li WH, He Q, Zhang ST, Pei CL, Hou BR (2008) J Appl Electrochem 38(3):289
26. Avci G (2008) Mater Chem Phys 112(1):234
27. Castellan GW (1984) Physical chemistry, 2nd edn. Addison-Wesley, Reading, MA
28. Olivares-Xometl O, Likhanova NV, Martínez-Palou R, Domínguez-Aguilar MA (2009) Mater Corros 60(1):14
29. Babić-Samardžija K, Lupu C, Hackerman N, Barron AR, Luttge A (2005) Langmuir 21(26):12187
30. Lashkari M, Arshadi MR (2004) Chem Phys 299(1):131
31. Khaled KF (2008) Electrochim Acta 53(9):3484
32. Khaled KF, Amin MA (2009) Corros Sci 51(9):1964