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ORIGINAL ARTICLE

Experimental and computational studies of *Nicotiana tabacum* leaves extract as green corrosion inhibitor for mild steel in acidic medium

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Mulliken charges

Abstract In the present work corrosion inhibition of mild steel in 2 M H_2SO_4 solution by *Nicotiana tabacum* extract was studied by weight loss method. It has been found that the extract acts as an effective corrosion inhibitor for mild steel in Sulfuric acid medium. The inhibition process is attributed to the formation of an adsorbed film of inhibitor on the metal surface which protects the metal against corrosion. The inhibition efficiency (%IE) and surface coverage (θ) of *N. tabacum* extract increased with increase in inhibitor concentration but decreased with increasing the temperature. The adsorption of extract on the mild steel surface was found to obey Langmuir's adsorption isotherm. The free energy value (ΔG_{ads}) indicated that the adsorption of inhibitor molecules was typical of physisorption. The results obtained show that *N. tabacum* Extract could serve as an excellent eco-friendly green corrosion inhibitor. Quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ) and Mulliken charges were calculated. Quantum chemical calculations also supported experimental data and the adsorption of inhibitor molecules onto the metal surface.

1. Introduction

Mild steel has been the most widely used alloy for structural and industrial applications such as, industries mining, construction and metal processing equipment [1]. The use of acid media in the study of corrosion of mild steel has become important because Sulfuric acids and Hydrochloric acid are the medium generally being used for pickling mild steel and industrial cleaning, and acid descaling [2,3]. The protection of metal against corrosion is a major industrial problem. The use of inhibitors is one of the best options of protecting metals against corrosion in acid solutions. Most organic compounds having heteroatoms and shows anti-corrosive activity [4]. Synthesis of these organic compounds is not only expensive but also toxic to both human beings and environments [2–5].

Thus, the researchers have been focused on the use of eco-friendly compounds and ecologically acceptable such as

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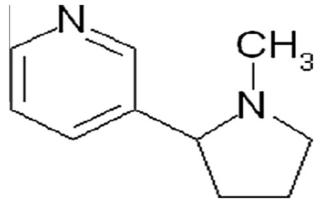

Figure 1 Basic structure of nicotine.

extract of common plants because these plant extracts are biodegradable, cheap, easy available and renewable sources of materials [6]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds [7,8]. Extracts of plant materials contain a wide variety of organic compounds. Most of them contain heteroatoms such as P, N, S, and O. These atoms coordinate with the corroding metal atom (their ions), through their electrons and prevent corrosion by formation of protective layer on the metal surface [8]. A great number of scientific studies have been dedicated to the corrosion inhibition of mild steel in acidic media by natural products as corrosion inhibitors [1,3,4,6–8].

Nicotiana tabacum is perennial herbaceous plant and member of Solanaceae family. It has been reported to extract contain relatively high concentrations of alkaloids, fatty acids and nitrogen-, fluorine-, sulfur- and oxygen-containing compounds [9]. Recently GC/MS analysis performed by Njoku and co-researchers [9] and determined the major phytochemical constituent present in *N. tabacum* is nicotine, which can be acted as an active constituent and extract use as inhibitor (Fig. 1). To explore this possibility, an attempt has been made to ascertain its corrosion inhibition properties on mild steel in 2 M H_2SO_4 solution by weight loss method and computational method also.

2. Experimental work

2.1. Preparation of leaves extract

N. tabacum (Tobacco) leaves were used to make the aqueous extract. Tobacco purchased from local market, dried leaves powder weighed 25 g were thoroughly washed in distilled water and soked in 250 mL. distilled water for 24 hours then heated at 50–55 °C and extract was filtered through Whattman No. 1 filter paper. The extract of tobacco leaf obtained in this manner was used as an inhibitor.

2.2. Preparation of test solution

The aggressive solution (2 M H_2SO_4) was prepared by dilution of Analytical Grade 98% H_2SO_4 with double-distilled water. The solution volume was 100 mL with and without the addition of different concentrations of *N. tabacum* extract ranging from 2.5 g/L to 10 g/L.

2.3. Specimen preparation

Prior to all measurements, the mild steel samples were polished with different emery papers up to 300 grade, and rectangular specimen of mild steel was mechanically pressed cut to form different coupons, each of dimension exactly $4 \times 2 \times 0.1$ cm. Each coupon was degreased by washing with double distilled water then dried in acetone and preserved in a desiccator. All reagents for the present study were Analar grade and double distilled water was used for their preparation.

2.4. Weight Loss method

The Weight Loss technique is the conventional and simplest of all corrosion monitoring techniques. The method involves exposing a specimen of material (the coupon) to a process environment for a given period, then removing the specimen for measurement. The basic measurement which is determined from corrosion coupons is weight loss, the weight loss taking place over the period of exposure being expressed as corrosion rate [10,11].

In the Weight loss measurements, mild steel coupons in triplicate were completely immersed in 100 mL of the test solution of acidic environment (2 M H_2SO_4) in the presence and absence of the inhibitor at different temperatures. The metal specimens were withdrawn from the test solutions after 6 h at temperature 303 K ± 1 and 313 K ± 1. The polished samples were cleaned with acetone. The Weight loss was taken as the difference in weight of the specimens before and after immersion determined using DHONA 200 D analytical balance with sensitivity of ±0.1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the weight loss is reported. Triplicate samples were used to check reproducibility of results. Weight loss allowed us to calculate the mean corrosion rate as expressed in mg cm^{-2} h^{-1}. Corrosion rate is calculated assuming uniform corrosion over the entire surface of the coupons. Corrosion rates, *CR* are calculated from weight loss methods. The formula used to calculate corrosion rate is as in Eq. (1). From the weight loss measurements, the corrosion rate will be calculated using the following relationship [10,11].

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \times W}{DAT} \tag{1}$$

where mmpy = millimeter per year, W = weight loss (mg), D = density (gm/cm^3), A = area of specimen (cm^2), and T = time in hours.

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using Eqs. (2) and (3), respectively.

$$\%\text{IE} = \frac{(W1 - W2)}{W1} \times 100 \tag{2}$$

$$\theta = \frac{(W1 - W2)}{W1} \tag{3}$$

where $W1$ and $W2$ are the corrosion rates in the absence and presence of the inhibitor respectively.

2.5. Quantum chemical study

Quantum chemical calculations based on DFT/B3LYP level are performed to find the relation between the molecular structure of the inhibitor and the inhibition efficiency. All the calculations were performed with Gaussian 03 for windows [12]. The molecular structure of Nicotine was fully and geometrically optimized using the functional hybrid B3LYP (Becke, three-parameter, Lee–Yang–Parr exchange correlation function) Density function theory (DFT) formalism with electron basis set 6-31G (d) for all atoms. The quantum chemical parameters obtained were total energy, E_{HOMO}, E_{LUMO}, energy gap (ΔE), dipole moment (μ) and Mulliken charges.

3. Results and discussion

3.1. Weight loss method

The effect of addition of *N. tabacum* extract tested at different concentrations on the corrosion of mild steel in 2 M H_2SO_4 solution was studied by weight loss measurements at 303 K and 313 K after 6 h of immersion period. The values of percentage inhibition efficiency (%IE) and corrosion rate obtained from weight loss method at different concentrations of *N. tabacum* extract at 303 K and 313 K are summarized in Tables 1 and 2. It is observed that the decreasing corrosion rate is associated with increase in the inhibitor concentration which indicates, adsorption of inhibitor on the metal surface or at the solution interface on increasing its concentration and providing wider surface coverage.

The corrosion rate values of mild steel decrease when the inhibitor concentration increases while %IE values of *N. tabacum* extract increase with the increase of the concentration reaching a maximum value of 94.13% at a concentration of 10 g/L at 303 K and 80.92% at a concentration of 10 g/L at 313 K. This behavior can be attributed to the increase of the surface covered (θ) and that due to the adsorption of phytochemical components of the *N. tabacum* extract onto the mild steel surface resulting in the blocking of the reaction sites, and protection of this surface from the attack of the corrosion active ions in the acid medium. Consequently, we can conclude that the *N. tabacum* extract is a good corrosion inhibitor for mild steel in 2 M H_2SO_4 solution. Figs. 2 and 4 show the variation of Inhibition efficiency versus inhibitor concentration at 303 K and 313 K respectively while Figs. 3 and 5 show the variation of corrosion rate versus inhibitor concentration at 303 K and 313 K respectively.

Table 1 Gravimetric results of mild steel in 2 M H_2SO_4 in the absence and presence of different concentrations of *Nicotiana tabacum* extract for 6 h at 303 K.

Concentration of inhibitor (g/L)	Weight loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%IE)	Surface coverage (θ)
BLANK	1928	448.22	–	–
2.5 g	385	89.50	80.03	0.80
5 g	227	52.77	88.22	0.88
7.5 g	170	39.52	91.18	0.91
10 g	113	26.27	**94.13**	0.94

Bold values indicate highest inhibition efficiency.

Table 2 Gravimetric results of mild steel in 2 M H_2SO_4 in the absence and presence of different concentrations of *Nicotiana tabacum* extract for 6 h at 313 K.

Concentration of inhibitor (g/L)	Weight loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%IE)	Surface coverage (θ)
BLANK	1987	461.94	–	–
2.5 g	630	146.46	68.29	0.68
5 g	560	130.19	71.81	0.71
7.5 g	410	95.31	79.36	0.79
10 g	379	88.11	**80.92**	0.80

Bold values indicate highest inhibition efficiency.

3.2. Effect of temperature

The dissolution behavior of mild steel in 2 M H_2SO_4 solution containing different concentrations of *N. tabacum* extract for 6 h at various temperatures such as 303 K and 313 K is studied and the results are shown in Figs. 2–5. The data of corrosion rates and corresponding efficiency (%IE) calculated were presented in Tables 1 and 2 at both temperature. The data obtained suggest that *N. tabacum* extract get adsorbed on the metal surface at both temperatures studied and corrosion rates increased with increase in temperature in 2 M H_2SO_4 solution. In acidic media, corrosion of metal is generally accompanied with evolution of H_2 gas, rise in temperature usually accelerates the corrosion reactions which results in higher dissolution rate of the metal [2]. Inspection of Table 3 showed that corrosion rate increased with increasing temperature both in uninhibited and inhibited solutions while the inhibition efficiency of *N. tabacum* extract decreased with temperature. It is due to weakening of physical adsorption.

The mechanism of corrosion protection may be explained on the basis of adsorption behavior. Adsorption isotherms are very important in determining the mechanism of organo-

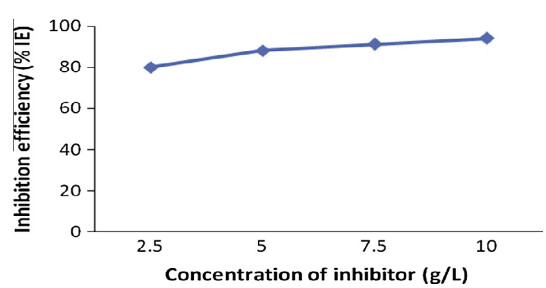

Figure 2 Concentration of inhibitor (g/L) and inhibition efficiency (%IE) of mild steel in various concentration of *Nicotiana tabacum* extract oil at 303 K in 2 M H_2SO_4 solution.

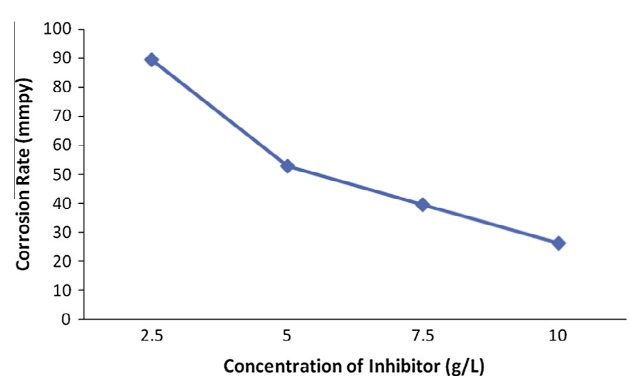

Figure 3 Concentration of inhibitor (g/L) and corrosion rate of mild steel in various concentration of *Nicotiana tabacum* extract oil at 303 K in 2 M H_2SO_4 solution.

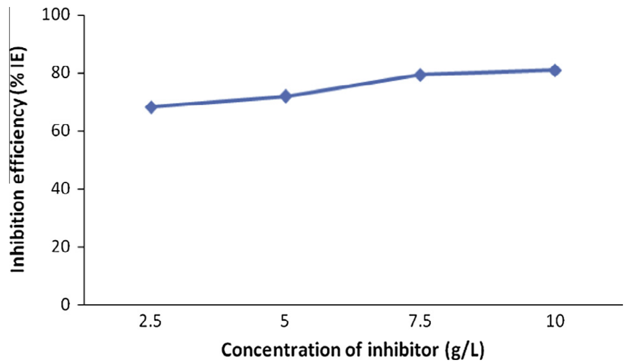

Figure 4 Concentration of inhibitor (g/L) and Inhibition efficiency (%IE) of mild steel in various concentration of *Nicotiana tabacum* extract oil at 313 K in 2 M H_2SO_4 solution.

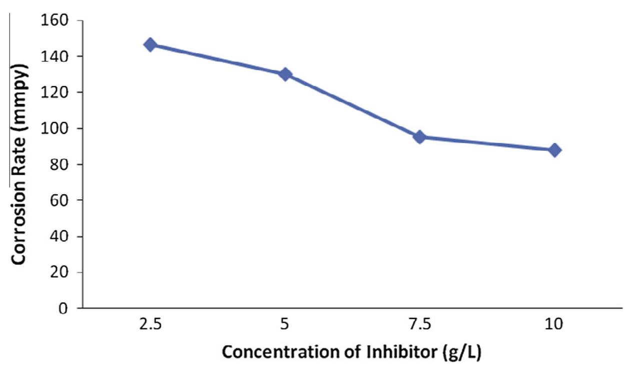

Figure 5 Concentration of inhibitor (g/L) and Corrosion rate (CR) of mild steel in various concentration of *Nicotiana tabacum* extract oil at 313 K in 2 M H_2SO_4 solution.

electrochemical reactions. The adsorptive behavior of a corrosion inhibitor is an important part of this study, as it provides important clues to the nature of the metal-inhibitor interaction. Interaction information between the inhibitor molecule and metal surface can be provided by adsorption isotherm. The adsorption of corrosion inhibitors at the metal/solution interface is due to the formation of either electrostatic or covalent bonding between the adsorbates and the metal surface atoms [13]. Langmuir adsorption isotherm was found to best describe the adsorption mechanism for *N. tabacum* extract as it fits the experimental results at 303 K and 313 K [14].

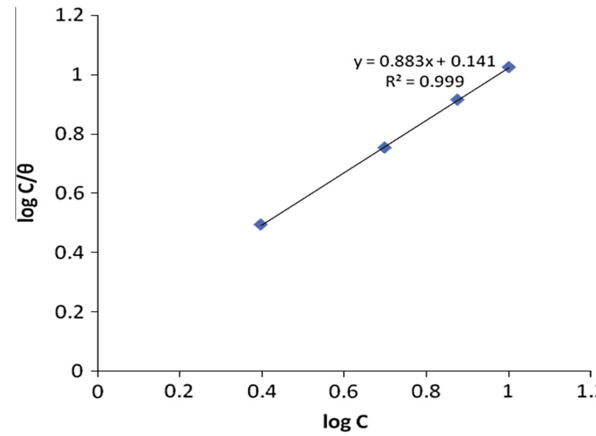

Figure 6 Langmuir adsorption isotherm plot for the adsorption of different concentrations of *Nicotiana tabacum* extract on the surface of mild steel in 2 M H_2SO_4 solution for 6 h at 303 K.

3.3. Adsorption studies

The Langmuir adsorption isotherm can be expressed by the Eq. (4) given below.

$$\log\frac{C}{\theta} = \log C - \log K \qquad (4)$$

where inhibitor concentration is C, the fraction of the surface covered (θ),adsorption coefficient K_{ads}. The linear graph between $\log C/\theta$ versus $\log C$ was (Figs. 6 and 7) indicating Langmuir adsorption.

Langmuir isotherm assumes that the metal surface contains a fixed number of adsorption sites and each site holds one adsorbate. Since the linear regression coefficient/or correction factors (R^2) are almost unity (0.999) at 303 K and (0.997) at 313 K, the adsorption behavior is believed to have obeyed Langmuir adsorption isotherms.

It is showed in the literature that the adsorption of heterocyclic compounds occurs with the aromatic rings mostly perpendicular with respect to the metal surface at low concentration, but at elevated inhibitor concentration the molecules are reoriented to the parallel mod. Besides, the adsorption phenomenon may be made by the *N. tabacum* extract. But as the extract contains so many components, the inhibitory action may also be due to synergistic intermolecular of the active molecules of this extract [15].

Table 3 Comparative results of Corrosion rate (CR) and Inhibition efficiency (%IE) of mild steel in 2 M H_2SO_4 in the absence and presence of different concentrations of *Nicotiana tabacum* extract for 6 h at 303 K and 313 K respectively.

Concentration of inhibitor (g/L)	303 K		313 K	
	Corrosion rate (mmpy)	Inhibition efficiency (%IE)	Corrosion rate (mmpy)	Inhibition efficiency (%IE)
BLANK	448.22	–	461.94	–
2.5 g	89.50	80.03	146.46	68.29
5 g	52.77	88.22	130.19	71.81
7.5 g	39.52	91.18	95.31	79.36
10 g	26.27	**94.13**	88.11	**80.92**

Bold values indicate highest inhibition efficiency.

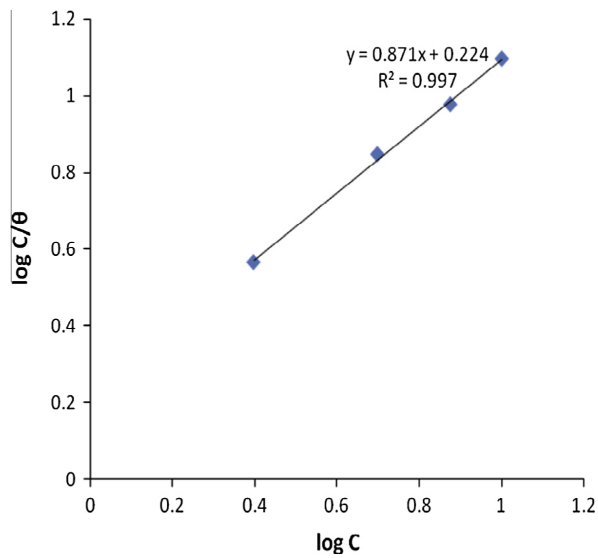

Figure 7 Langmuir adsorption isotherm plot for the adsorption of different concentrations of *Nicotiana tabacum* extract on the surface of mild steel in 2 M H_2SO_4 solution for 6 h at 313 K.

3.4. Free energy determination

The free energies of adsorption, ΔG_{ads}, were calculated from the equilibrium constant of adsorption using the following equation [13]:

$$\Delta G_{ads} = -2.303RT\log[55.5K_{ads}] \tag{5}$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant and T is the absolute temperature [13].

Generally, values of ΔG_{ads} around −20 kJ/mol or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal [physisorption], those around −40 kJ/mol or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond [13]. The value of ΔG_{ads} reflects the weak adsorption capability. The negative values of ΔG_{ads} showed (Table 4) that the adsorption of inhibitor molecules on the metal surface is spontaneous. $\log K_{ads}$ values were obtained from the slope of graph plotted between $\log C/\theta$ and $\log C$. The values of ΔG_{ads} obtained were $-9.80\ \text{kJ mol}^{-1}$ at 303 K and $-10.09\ \text{kJ mol}^{-1}$ at 313 K for *N. tabacum* extract. Accordingly, the values of ΔG_{ads} obtained in the present study indicate that the adsorption mechanism of *N. tabacum* extract on mild steel is simply physisorption, thus inhibitor protection is through film formation providing an unbreakable barrier against aggressive ions of the electrolyte (see Table 5).

Table 4 Free energy value at 303 K and 313 K.

Temperature (K)	Slope	K_{ads}	$-\Delta G_{ads}$ (kJ mol^{-1})
303	0.883	49.00	−9.80
313	0.871	48.34	−10.09

Table 5 Calculated quantum chemical parameters of studied inhibitor.

Quantum chemical parameters	Nicotine
HOMO (Hartree)	−0.336
LUMO (Hartree)	−0.205
ΔE (LUMO–HOMO)	0.131
Dipole moment (μ)	3.457 Debye
Total energy (a.u.)	−498.97

3.5. Quantum chemical calculations

Quantum chemical calculations were carried out in order to investigate adsorption and inhibition mechanism of studied inhibitor molecules [12]. Fig. 8 shows full geometry optimization of the inhibitor molecules. The Frontier molecular orbital (FMO) density distributions of Nicotine present in *N. tabacum leaves* extract are shown in Fig. 9. In order to construct a composite index of an inhibitor molecule it may be important to focus on parameters that directly influence the electronic interaction of the inhibitor molecules with the metal surface. These are mainly: *E*HOMO, *E*LUMO, Δ*E* (*E*LUMO–*E*HOMO), dipole moment (μ) and Mulliken charges (Table 4). As *E*HOMO is often associated with the electron donating ability of a molecule, high values of *E*HOMO are shown a tendency of the molecule to donate electrons to appropriate acceptor molecules with low-energy, empty molecular orbital. Increasing values of the *E*HOMO alleviate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer. Therefore, the energy of the *E*LUMO shows the ability of the molecule to accept electrons; hence these are the acceptor states. The lower the value of *E*LUMO, the more probable, it is that the molecule would accept electrons [16]. As for the values of ΔE (*E*LUMO–*E*HOMO) concern; lower values of the energy difference ΔE will cause higher inhibition efficiency because the energy to remove an electron from the last occupied orbital will be low [17]. The higher values of dipole moment (μ) favor accumulation of the inhibitor in the surface layer. The estimation of the total energy gives good information, the higher total energy (−498.97 a.u.) confirms the higher stability of Nicotine molecule [18]. The Mulliken charges of Nicotine molecule are shown in Table 6. The highest negative charge is domiciled in Nitrogen atom. There is a general consensus by several authors that the more negatively charged heteroatom is, the more is its ability to adsorb on the metal surface [19,20].

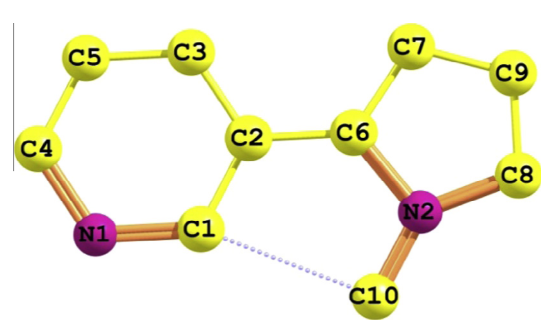

Figure 8 Optimized structure of studied molecule Nicotine.

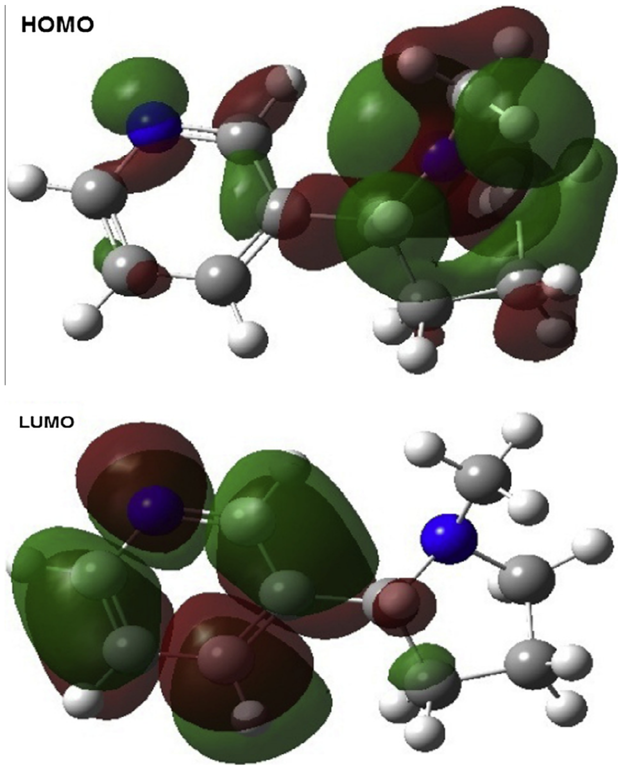

Figure 9 Schematic representation of HOMO and LUMO molecular orbital of the studied molecule Nicotine.

Table 6 Mulliken atomic charges on studied Nicotine molecule.

S. No.	Atom	Mulliken charges
1	C	−0.03162
2	C	0.151574
3	**N**	**−0.392874**
4	C	−0.297403
5	C	−0.153801
6	C	−0.013474
7	C	−0.129346
8	C	−0.312939
9	C	−0.280379
10	C	−0.135546
11	**N**	**−0.418896**
12	C	0.035758
13	H	0.13806
14	H	0.149857
15	H	0.142025
16	H	0.133066
17	H	0.154303
18	H	0.140028
19	H	0.143716
20	H	0.155051
21	H	0.152911
22	H	0.123445
23	H	0.140103
24	H	0.137075
25	H	0.133029
26	H	0.136279

Bold values indicate highest inhibition efficiency.

4. Conclusions

The active molecule nicotine present in the plant extract effectively inhibited the corrosion of mild steel in 2 M H_2SO_4 by forming a protective barrier layer. It adsorbs on the mild steel surface according to the modified Langmuir adsorption isotherm. The %IE and corrosion resistance of the mild steel increased with inhibitor concentrations and inhibition efficiency and degree of surface coverage decreases as temperature increases in acidic environments for weight loss method considered. The results of the weight loss were all in very good agreement to support the above conclusions. The adsorption behavior of the *N. tabacum* extract in acidic media for mild steel can be said to obey Langmuir adsorption isotherm. The negative values of ΔG_{ads} show that adsorption of inhibitor on surface of mild steel is spontaneous. The *N. tabacum* extract can be considered as a source of relatively cheap, eco-friendly, biodegradable and effective acid corrosion inhibitors. Quantum chemical approach is adequately sufficient to predict the structure and molecule suitability to be an inhibitor.

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