

## Experimental and Theoretical Studies on the Corrosion Inhibition of Mild Steel in Acidic Media by *Pentaclethra Macrophylla* Plant Extract

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### Abstract

The inhibition of corrosion of mild steel in 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions by the leaves extracts of *Pentaclethra macrophylla* (PM) was investigated using the gravimetric technique at 30–60 °C. It was found that PM extracts acted as an inhibitor for acid-induced corrosion of mild steel. The inhibition efficiency (IE %) of the extract increased with increase in extract concentration reaching a maximum of 89 % in both 1M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub>. Furthermore, inhibition efficiency (IE %) increased with increase in temperature and synergistically on addition of potassium iodide. Inhibitor adsorption characteristics were approximated by Langmuir adsorption isotherm at all the concentrations studied. The mechanism of chemical adsorption is proposed from the trend of inhibition efficiency with temperature. Quantum chemical calculations were performed using the density functional theory to find out whether a clear link existed between the inhibitive effect of the extract and the electronic properties of its main constituent.

**Keywords:** Corrosion inhibitor, mild steel, molecular modeling, *pentaclethra macrophylla*.

### 1.0 Introduction

Different organic and non-organic compounds have been studied as inhibitors to protect metal from corrosion attack. Organic compounds containing functional electronegative groups and  $\pi$ -electrons in triple bonds are found to be effective corrosion inhibitors for many metal and alloys (Jones, 1998; Sastry, 1998; Quraishi *et al*, 2002; Ju *et al*, 2008;). The inhibition efficiency of organic compounds are strongly dependent on the structure and chemical properties of the layer formed on the metal surface under particular experimental conditions (Samide *et al*, 2005, 2009; Bentiss *et al*, 2000). Available results show that most inhibitors act by adsorption on the metal surface (Solmaz *et al*, 2008; Gerengi *et al*. 2012; Fang & Li, 2002). The strength of adsorption and hence, the extent of inhibition are dependent on the nature organic compound, metal and the corrosive media.

Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. Because of the general aggressive nature of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. The development of inhibitors for steel in acid solutions has been the subject of great interest especially from the point of view of their efficiency and applications. Acidization of petroleum oil well is one of the

important stimulation techniques for enhancing oil production. It is brought about by using a solution of 15–28% hydrochloric acid. To reduce the aggressive attacks of acid on tubing and casing materials, inhibitors are incorporated to acid solution during acidizing process (Abd El-Maksoud, 2008).

The study of corrosion processes and their inhibition by natural products especially of plant origin is a very active field of research (Martinez *et al*, 2003; Foad, 1999; Hussin *et al*, 2011; Gualdrón *et al*, 2013; Gupta *et al*, 2009, Gunasekaran *et al*, 2004; Bothi *et al*, 2008). The environmental requirements currently imposed on the development of cleaner chemical inhibitors represent a strong motivation for the study of inhibition by plant extracts.

Like the other organic inhibitors that act through adsorption to the metal surface the rationalization of tannin inhibitory action demands knowledge not only for the various electrochemical, kinetic and thermodynamic parameters of the corrosion system but also, the knowledge of the inhibitor molecular properties. Some quantum chemical studies have successfully linked the corrosion inhibition efficiency with molecular properties for different kinds of organic compounds (Roque *et al*, 2008; Bartley *et al*, 2003; Xia *et al*, 2008; Khaled, 2008; Cruz *et al*, 2005; Rodriguez-Valdez *et al*, 2005a).

*Pentaclethra macrophylla* (African oilbean) belongs to the family, leguminosae and generally found in the forest zones of West and Central Africa. All the parts of the plant are used for various animal and human medicines (Akah *et al*, 1999; Ugbogu & Akukwe, 2009). Extracts of the leaf, stem bark, seeds and fruit pulp have anti-inflammatory and anthelmintic activity, and are used to treat gonorrhoea and convulsion. The root bark is used as a laxative, and an enema against dysentery, and as a liniment against itch. Phytochemical analysis of the ethanolic extract of stem bark showed the presence of tannins alkaloids, glycosides, cyanogenic-glycosides, phenols and saponins (Idonije *et al*, 2011). The bark is a potential source of tannins for fur tanning. The seeds and leaves contain the growth-retardant alkaloid paucine (Fig. 1) as the major constituent (Allen & Allen, 1981; Flores, 1994). However, no parts of *Pentaclethra macrophylla* have been studied for the purpose of corrosion inhibition.

The aims of this paper are to investigate the inhibition efficiency of PM leaf extract using gravimetric technique and the synergistic effect of iodide ions addition; to explain the ability the major active constituent to act as corrosion inhibitor using density functional theory (DFT) calculations. The molecular structure and the electronic parameters that can be obtained through such calculations such as the highest occupied molecular orbital (HOMO) energy, the LUMO lowest unoccupied molecular orbital (LUMO) energy, and the energy gap ( $\Delta E = E_{LUMO} - E_{HOMO}$ ), are involved in the reactivity of the molecule (Rodriguez-Valdez *et al*, 2006; Cruz *et al*, 2005; Rodriguez-Valdez *et al*, 2005).

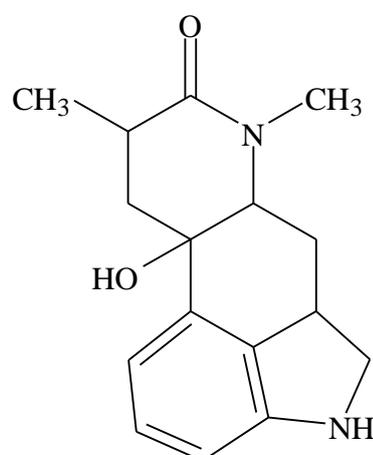


Figure 1. Chemical Structure of Paucine

## 2.0 Materials and methods

### 2.1. Preparation of electrolyte

All reagents were BDH grade, and used as source without further purification. Distilled water was used for all solution preparations. 1.0 M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> solution were employed as blank solutions.

### 2.2. Preparation of plant Extract

PM leaves were collected from one of the trees adorning the main gate to Federal University of Technology, Owerri (FUTO), and identified at the Department of Crop Science Technology. The air dried plant material was ground and stored in airtight container prior to use. Stock solutions of the PM extract were prepared by refluxing 25g of the dried and ground PM leaves in 1 dm<sup>3</sup> of 1M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> solutions respectively for 3 h. The resulting solution was filtered and the residue obtained was dried to constant weight and used to determine the amount of plant material extracted in the acid solution. The concentration range of inhibitor (PM extract) for this study varied from 2 to 500 mg/L. For experiments that involved halide additive, 5.0 mM KI were prepared in the blank solution and in the solutions containing 25 and 50 mg/L of PM extract respectively.

### 2.3. Weight loss experiment

Weight loss measurements were carried out using mild steel specimen containing 0.05 % C, 0.30 % Si, 0.50 % Mn, 0.36 % P, 0.004 % S and the remaining, Fe. The dimensions of the rectangular specimen were 3 x 3 x 0.15 cm. The surface preparation of the specimens was accomplished by using different grades of emery paper and subsequent cleaning with distilled water and acetone. Weight loss measurements were conducted under total immersion using 300 ml glass bottles containing 200 ml test solution without and with different concentrations of the extract at 30 °C. The mild steel coupons were retrieved after 6 h, rinsed severally with distilled water, cleaned and dried in acetone and reweighed. The tests were repeated at 40, 50 and 60 °C for 3 h immersion time. The experiments were carried out in triplicates to ensure reproducibility and the average value of the weight loss was noted. The inhibition efficiency (IE %), and surface coverage ( $\theta$ ) were determined using the following equations:

$$(\theta) = \frac{w_o - w_i}{w_o} \quad (1)$$

$$\text{I.E (\%)} = \frac{w_o - w_i}{w_o} \times 100 \quad (2)$$

where  $w_i$  and  $w_o$  are the weight loss values in the presence and absence of inhibitor, respectively.

The corrosion rate ( $C_R$ ) of mild steel was calculated using the relation:

$$C_R (\text{mdd}) = \frac{\Delta w}{st} \quad (3)$$

where,  $\Delta w$  is the average weight loss of the coupons (mg),  $s$  is the total area of the mild steel coupon (dm<sup>2</sup>) and  $t$  is the immersion time (days).

### 3.0 Results and Discussion

#### 3.1. Weight loss studies

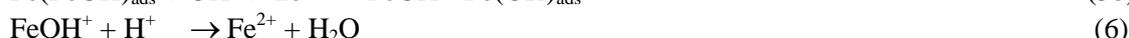
##### 3.1.1. Effect of concentration

The values of weight loss (WL) and corrosion rate (CR) obtained from gravimetric experiment at different concentrations of PM extract in 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> at 30°C for 6 h immersion period are summarized in Table 1. The data in Table 1 show higher corrosion rate of the mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> solution compared to 1M HCl solution, even though both solutions have identical anion concentration.

Table 1: Average weight loss (AWL) and corrosion rate (CR) for mild steel in aqueous solutions of 1 M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentrations of PM extract at 30°C.

Conc. (mg/L)	1 M HCl		0.5 M H <sub>2</sub> O <sub>4</sub>	
	AWL (g)	CR (mdd)	AWL (g)	CR(mdd)
Blank	0.0100	418.400	0.1129	4726.40
2	0.0190	377.110	0.0480	2009.60
5	0.0160	344.120	0.0263	1100.80
10	0.0940	321.110	0.0187	783.20
25	0.0076	318.200	0.0182	761.60
50	0.0058	243.200	0.0180	753.60
75	0.0040	167.200	0.0174	728.80
100	0.0040	167.200	0.0174	728.80
150	0.0026	108.800	0.0134	560.80
200	0.0021	88.000	0.0130	548.80
300	0.0011	46.400	0.0128	549.00
400	0.0012	50.250	0.0133	555.40
500	0.0014	58.620	0.0142	594.63

This observation can be attributed to the role of the acid anion in the corrosion process. The anodic dissolution of iron in acidic solutions has been reported to proceed according to the mechanism (Bala, 2004):



In addition to the catalytic activity of OH<sup>-</sup> ions, other anions such as Cl<sup>-</sup>, I<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and S<sup>2-</sup> may also participate in forming reaction intermediates on the corroding metal surface which either inhibit or promote corrosion. Halide ions are particularly known to have the tendency to replace OH<sup>-</sup> ions adsorbed on the metal surface thereby reducing their catalytic activity hence, the corrosion rate decreases. Such an effect is not so pronounced with SO<sub>4</sub><sup>2-</sup> ions (Bala, 2004; Oguzie *et al.*, 2008).

Fig. 2 compares the trend of inhibition efficiency of PM extract in the two corrodents being studied and it showed a more gradual rise in IE% in 1 M HCl from 3.0 % at 2 mg/L concentration reaching a maximum of 89.0 % at 300 mg/L. The H<sub>2</sub>SO<sub>4</sub> medium showed a more abrupt increase in IE% from 57.5 % at 2 mg/L concentration to reach a maximum of 89.9 % at 200 mg/L. Further increase in extract concentration did not lead to any significant change in the performance of the extract.

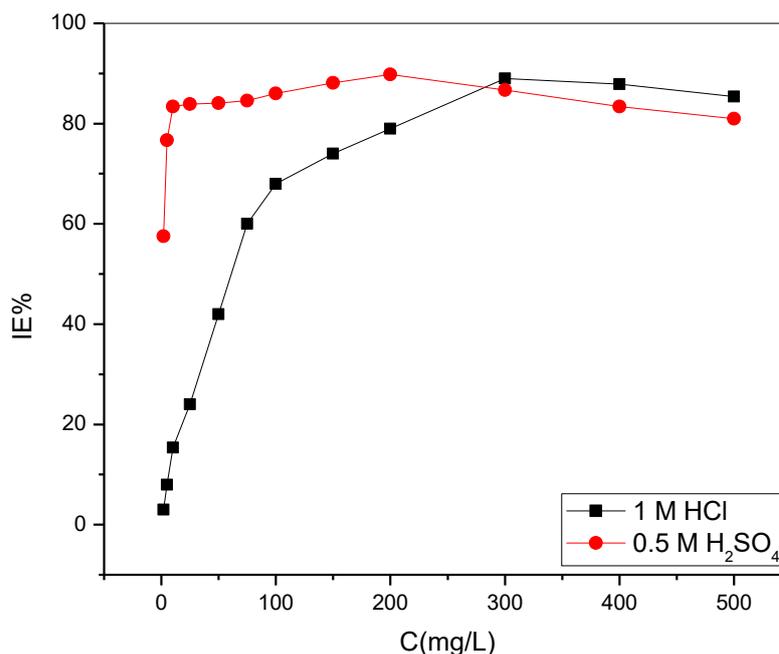


Figure 2. Trend of inhibition of PM extract with concentration for mild steel corrosion in 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub>

### 3.1.2. Effect of temperature

In order to understudy the temperature dependence of corrosion rates in uninhibited and inhibited solutions, gravimetric measurements were carried out in the temperature range 30-60°C in the absence and presence of 25 mg/L and 300 mg/L PM extract in both 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions. The calculated values of the corrosion rates and inhibition efficiencies are shown in Table 2. Inspection of the data shows that the corrosion rate of mild steel in all systems studied increased with temperature, though the effect was significantly reduced in the inhibited solutions, an indication that the degree of adsorption of PM extract on mild steel surface also increased increase in temperature. The enhanced inhibitor adsorption at higher temperatures was manifested in the increasing inhibition efficiency with rise in temperature; an indication that some of the extract components were better adsorbed at higher temperature and so contributes significantly to the overall inhibition effect. Figures 3 show the variation of inhibition efficiency of PM extract with temperature.

Table 2. Variation of temperature (K) with corrosion rate (CR) of mild steel in 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions without and with PM extract

T (K)	Conc.(mg/L)	1M HCl	0.5M H <sub>2</sub> SO <sub>4</sub>
		CR(mdd)	CR(mdd)
303	25	318.40	761.60
	300	46.400	549.00
	Blank	418.200	4726.40
313	25	1385.00	2215.24
	300	397.600	883.58
	Blank	5572.00	19434.67
323	25	1385.00	3107.20
	300	699.200	871.02
	Blank	13622.01	37328.30
333	25	18021.60	3546.60
	300	3252.80	615.57
	Blank	42464.44	56280.00

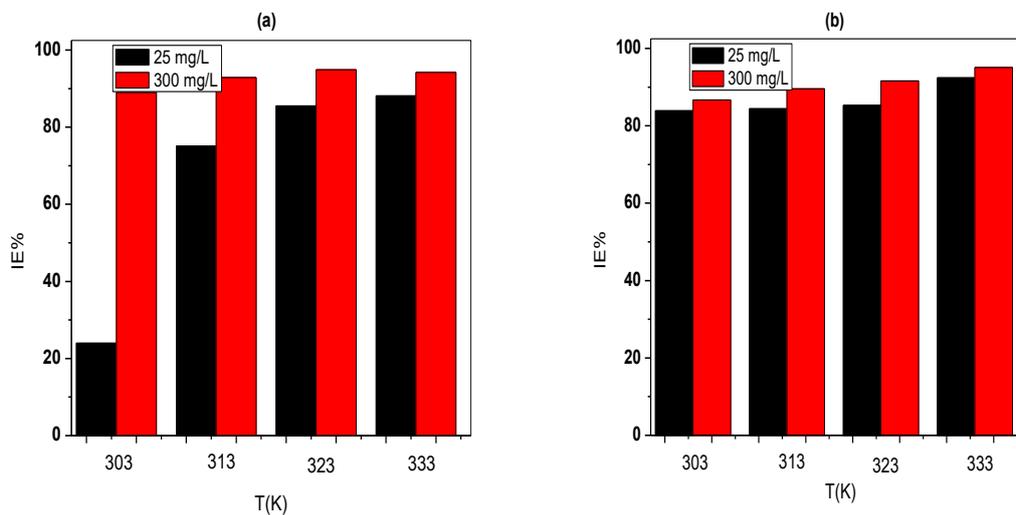


Figure 3: Variation of inhibition efficiency with temperature for PM extracts in (a) 1 M HCl and (b) 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions.

The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation (Zhang *et al.*, 2012):

$$\log C_R = \frac{-E_a}{2.303RT} + A \tag{7}$$

where  $E_a$  is the apparent effective activation energy,  $R$  is the general gas constant and  $A$  is the Arrhenius pre-exponential factor. A plot of  $\log$  of corrosion rate vs.  $1/T$  gave a straight line as shown in Figure 4 with a slope of  $-E_a/2.303R$ .

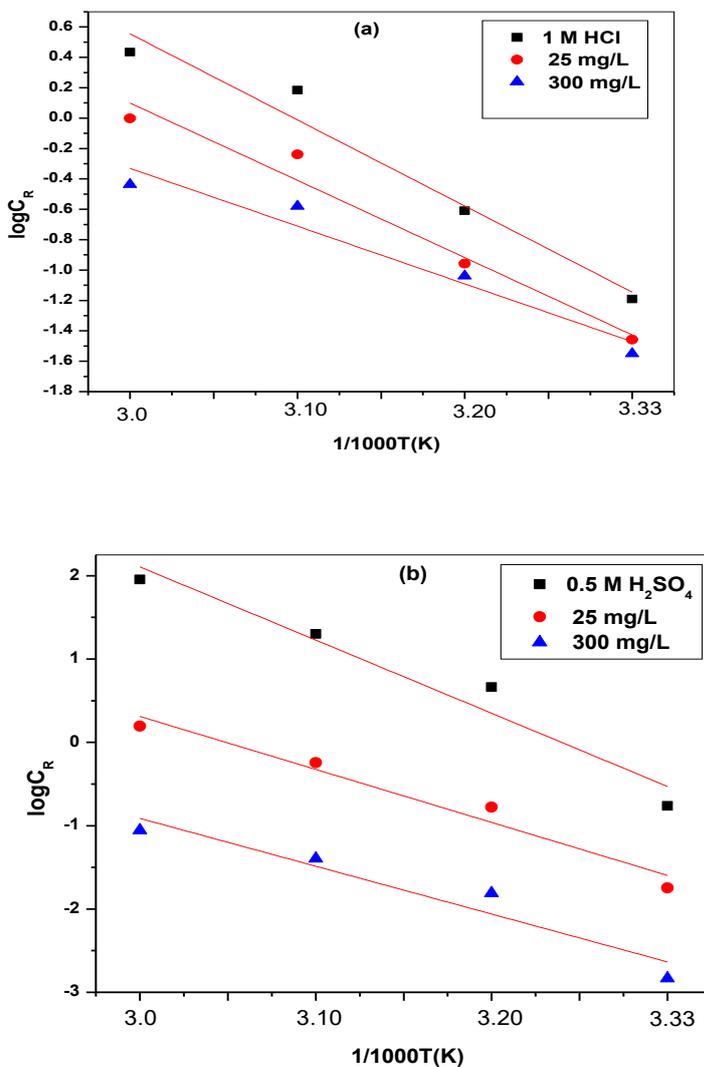


Figure 4: Arrhenius plots for mild steel corrosion in (a) 1 M HCl and (b) 0.5 M  $H_2SO_4$  solutions without and with PM extract

The values of the activation energies are presented in Table 3. The data shows that the thermodynamic activation function ( $E_a$ ) for the corrosion of mild steel in 1M HCl and 0.5M  $H_2SO_4$  solutions in the presence of extract were lower than those in the free acid solutions an indication that the extract exhibited high IE (%) at elevated temperatures. This may suggest that the extract is more effective in inhibiting the acid corrosion of mild steel at higher temperatures.

Table 3: Values of the activation energies ( $E_a$ ) and heat of adsorption ( $Q_{ads}$ ) for mild steel corrosion in the presence and absence of PM extract

Conc. (mg/L)	1M HCl		0.5 M H <sub>2</sub> SO <sub>4</sub>	
	Ea(kJ/mol)	Qads (kJ/mol)	Ea(kJ/mol)	Qads (kJ/mol)
25	54.146	162.382	61.350	12.628
300	87.480	44.692	50.429	20.336
Blank	129.222	-	69.278	-

According to Popova et al. (2003), unchanged or lowered activation energies in inhibited solutions when compared to that in its absence indicates a specific type of adsorption of the inhibitors, while Szauer and Brandt (1981) associated this behaviour with the chemisorption of inhibitor to the metal surface. Thus, corrosion inhibition action of PM extract for mild steel in acidic solution can be attributed to the formation of a strong adsorption bond of a chemisorptive nature. An estimate of the heat of adsorption ( $Q_{ads}$ ) was obtained from the trend of surface coverage with temperature using the equation (Bhajiwal & Vashi, 2001; Gomma, 1998; Quraishi & Sardar, 2003):

$$Q_{ads} = 2.303R[\log(\theta_2/1-\theta_1)-\log(\theta_1/1-\theta_2)] \times T_1 T_2 / T_2 - T_1 \quad (8)$$

where  $\theta_1$  and  $\theta_2$  are the degrees of surface coverage at temperatures  $T_1$  and  $T_2$ . The calculated values of  $Q_{ads}$  are given in Table 3. The positive values of heats of adsorption ( $Q_{ads}$ ) indicate that the degree of surface coverage increased with rise in temperature, again suggesting that the effectiveness of PM as an inhibitor increases with increase in temperature (Bhajiwal & Vashi, 2001; Gomma, 1998; Quraishi & Sardar, 2003; Gomma & Wahdan, 1994; Makhoulouf *et al*, 1995).

### 3.1.3. Effect of halide additive.

It is generally accepted that halide ions facilitate adsorption of organic inhibitors during mild steel corrosion in acidic media by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor (Oguzie, 2008). Corrosion inhibition synergism then results from increased surface coverage arising from ion-pair interactions between the organic cations in solution and the specifically adsorbed halide ions on the metal surface (Martinez & Stagljar, 2003, Oguzie, 2008). Hence, if protonated species play a part in corrosion inhibition, a synergistic increase in efficiency should be observed in the presence of the halide additives, as shown in Table 4. The observed inhibiting effect of PM extract can be attributed to the involvement of both protonated and molecular species in the adsorption process. The slightly higher inhibition efficiency of the extract recorded in 0.5M H<sub>2</sub>SO<sub>4</sub> implies that chemisorption of molecular species made a significant contribution. Physisorption of protonated species becomes an important factor in 1M HCl, accounting for the lower inhibition efficiency observed. Inhibition efficiency in both corrodents increased on introduction of the halides as a result of improved adsorption of both molecular and protonated species of the inhibitor.

Table 4: Effect of the addition of 0.005M KI on the corrosion rate of mild steel in 1.0M HCl and 0.5M H<sub>2</sub>SO<sub>4</sub> without and PM addition

System	CR(mdd)	I.E%
1.0M HCl+25mg/L PM	318.0	24
1.0M HCl+50mg/L PM	243.0	42
1.0M HCl+25mg/L PM + KI	184.0	56
1.0M HCl+50mg/L PM + KI	155.2	63
0.5M H <sub>2</sub> SO <sub>4</sub> +25mg/L PM	2009	58
0.5M H <sub>2</sub> SO <sub>4</sub> +50mg/L PM	1190	77
0.5M H <sub>2</sub> SO <sub>4</sub> +25mg/L+ KI	1175	84
0.5M H <sub>2</sub> SO <sub>4</sub> +50mg/L+ KI	498	89

#### 3.1.4. Adsorption isotherm

The mechanism of corrosion inhibition can be deduced in terms of the adsorption characteristics of the inhibitor (Khaled, 2008, Larabi *et al.* 2006; Martinez *et al.* 2001). Metal surface in aqueous solution is always covered with adsorbed water dipoles. Therefore, the adsorption of inhibitor molecules from aqueous solution is a quasi-substitution process. A correlation between surface coverage ( $\theta$ ) and the concentration of inhibitor (C) in electrolyte can be represented by the Langmuir adsorption isotherm as (Bartley *et al.* 2003):

$$\frac{C}{\theta} = C + \frac{1}{K} \quad (9)$$

where, K is the adsorption constant.

The surface coverage ( $\theta$ ) values (Eq. 1) for the inhibitor were obtained from the weight loss measurements for the various concentrations studied at 30°C. The best fitted straight line was obtained for the plot of  $C/\theta$  versus C with slope of unity. The correlation coefficient ( $R^2$ ) was used to choose the isotherm that best fit the experimental data (Gomma 1998; Martinez & Stern, 2002, Beza *et al.* 2003; Pine, 1987; Oguzie *et al.* 2006, Bartley *et al.* 2003; Larabi *et al.* 2006). This result suggests that the adsorption of mild steel on metal surface followed the Langmuir adsorption isotherm (Fig. 5).

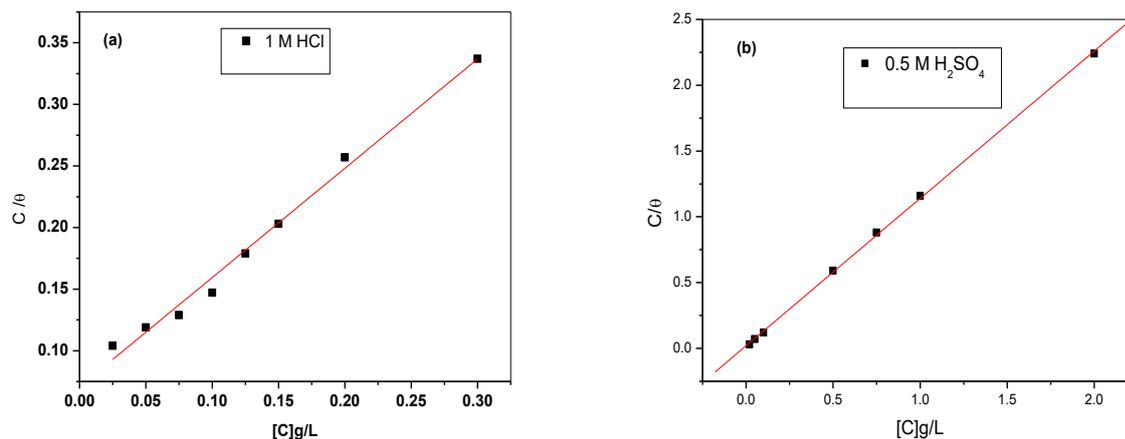
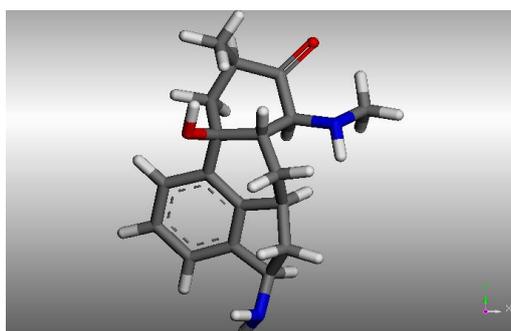


Figure 5. Langmuir adsorption isotherm for mild steel corrosion in (a) 1.0M HCl and (b) 0.5M H<sub>2</sub>SO<sub>4</sub>

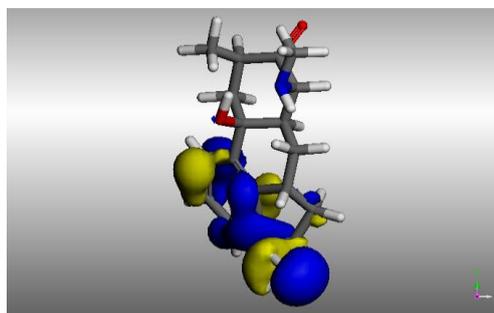
### 3.2. Quantum chemical calculations

Molecular modeling is based on the proposition that all the properties of the molecule are related to its molecular structure or geometry (Bartley *et al*, 2003; Cruz *et al*, 2004; Rodriguez-Valdez *et al*, 2005). Thus, in order to understand the adsorption behaviour of major active constituent of PM on mild steel, different electronic structure parameters, such as the energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ); the energy of the lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ); the gap energy  $\Delta E$  ( $E_{\text{LUMO}} - E_{\text{HOMO}}$ ) and the dipole moment ( $\mu$ ) were calculated. The calculations were performed using DFT electronic program Dmol3 involving a Mulliken population analysis. The electronic parameters for the simulation include unrestricted spin polarization using DND basis set and perdue-Wang (PW) local correlation density functional. The electronic structure of *paucine*, including the distribution of frontier molecular orbital and Fukui function and the structural parameters are presented in Figure 6 (a-c).

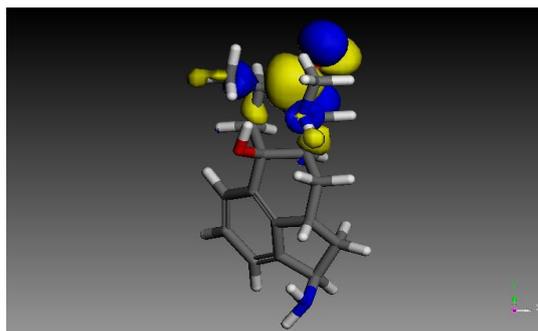
Table 5 provides some quantum-chemical parameters related to the molecular electronic structure of the most stable conformation of the paucine molecule.



(a)



(b)



(c)

Figure 6. Molecular orbital structures of Paucine (a) Optimized structure (b) HOMO density (c) LUMO density [Atomic legend: Gray = C; white = H; blue = N; red = O].

Table 5: Calculated quantum chemical properties of paucine

Parameter	Value
Total energy (eV)	-25900
$E_{\text{HOMO}}$ (eV)	-5.069
$E_{\text{LUMO}}$ (eV)	-3.566
$\Delta E$ (eV)	1.503
I(eV)	5.069
A(eV)	3.566
X(eV)	4.317
$\eta$ (eV)	0.756
$\mu$ (Debye)	1.53
$\Delta N$ (eV)	1.77

According to Frontier Orbital Theory, transition of electrons is due to the interaction of the frontier orbital of the reactants which in this case is the metal and the inhibitor. The HOMO energy can indicate the disposition of the molecule to donate electrons to an appropriate acceptor with an empty molecular orbital. Also, an increase in the values of  $E_{\text{HOMO}}$  can facilitate the adsorption and therefore, the inhibition efficiency (Cruz et al, 2004; Rodriguez-Valdez *et al*, 2005). The  $E_{\text{HOMO}}$  value of -5.07eV obtained for the molecule being studied suggested strong tendency for charge donation to the metallic surfaces and therefore an appreciable corrosion inhibition should be expected. Also, the low values of the gap energy ( $\Delta E$ ) could provide good inhibition efficiency because the excitation energy to remove an electro from the last occupied orbital will be low (Rodriguez-Valdez *et al*, 2005). The location of the HOMO in the molecule is around the indole ring suggesting the preferred site for electrophilic attack through which the molecule can interact with the metal surface. It is probable that the part of the molecule having high HOMO density was oriented to the metallic surface and the adsorption of this molecule could be by sharing the lone pair electrons and the  $\pi$ -electrons of the aromatic ring. On the other hand, the location of the LUMO around the benzoid nitrogen

atom indicates the site which can accept electrons from the 3d-orbital of the Fe atom to form feedback bonds, thus, further strengthening the interaction of inhibitor and Fe surface.

The Koopman's theorem (Martinez & Stagljar, 2003; Ju *et al*, 2008; Cruz *et al*, 2004; Rodriguez-Valdez *et al*, 2005a) establishes a relation between the energies of HOMO and LUMO and ionization potential and electron affinity of the inhibitor molecule respectively as,

$$I = -E_{\text{HOMO}} \quad (10)$$

$$A = -E_{\text{LUMO}} \quad (11)$$

The absolute electronegativity ( $\chi$ ) and absolute hardness ( $\eta$ ) of the inhibitor molecule are calculated in terms of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  as (Martinez & Stagljar, 2003):

$$\chi = (I+A)/2 \quad (12)$$

$$\eta = (I-A)/2 \quad (13)$$

In metal- inhibitor interactions, electrons move from the inhibitor to the metal d-orbital. The fraction of electrons transferred ( $\Delta N$ ) can be determined using the equation (Martinez & Stagljar, 2003; Ju *et al*, 2008):

$$\Delta N = (\chi_{\text{Fe}} - \chi_{\text{inh}})/2(\eta_{\text{Fe}} + \eta_{\text{inh}}) \quad (14)$$

where a theoretical electronegativity value of  $\chi_{\text{Fe}}=7.0\text{eV}$  is given for iron and absolute hardness of  $\eta_{\text{Fe}}=0$  is assumed, since I equals A for bulk metals (Martinez & Stagljar, 2003). Lukovits *et al*. (2001), observed that if  $\Delta N < 3.6$ , the inhibition efficiency increased with increasing electron-donating ability at the metal surface. The value  $\Delta N$  of 1.77eV obtained in this study indicates that paucine was the donor of electrons and the iron surface was the acceptor which agrees with Lutovits finding. Similarly, a low value of the dipole moment ( $\mu$ ) favours the accumulation of inhibitor molecules on the metal surface besides being an indicator of the hydrophobic character of the same molecule (Rodriguez-Valdez, 2005b).

### 3.2.2. Molecular Dynamics (MD) Simulation

In order to gain insight into the interaction between the inhibitor and the mild steel surface, a theoretical simulation of the adsorption of the paucine (inhibitor) molecule on the metal surface was performed. The MD calculations of the interaction between the inhibitor molecule and Fe surface was carried out in a simulation box (2.009 x 0.861 x 3.444 nm) with periodic boundary conditions to model a representative part of the interface devoid of any arbitrary effects. The Fe crystal was cleaved along the (110) plane with the upper most and lowest layers fixed. Temperature was fixed at 350 K, with NVE ensemble, with a time simulation time of 5ps. The force field used in the current MD is COMPASS (condensed phase optimized molecular potential simulation studies) force field. The binding energy per mole ( $E_{\text{Fe-inhibitor}}$ ) on the Fe surface was calculated according to the equation (Zhang *et al*, 2007; Xia *et al*. 2009):

$$E_{\text{Fe-inhibitor}} = E_{\text{Fe+inhibitor}} - E_{\text{Fe}} - E_{\text{inhibitor}} \quad (15)$$

where  $E_{\text{Fe+inhibitor}}$  is the total potential energy of the Fe crystal and the adsorbed inhibitor molecule,  $E_{\text{Fe}}$  and  $E_{\text{inhibitor}}$  are the total energies of the Fe crystal and the inhibitor molecule respectively.

Fig. 7 shows the optimized (lowest energy) adsorption model for a single paucine molecule on the Fe (110) surface from the simulation. Solvent and charge effects have been neglected.

The binding energy value obtained was positive (132 kcal/mole). Xia *et al.* (2009) obtained a similar result in a study on the relationship between the structure of imidazole derivatives and inhibition performance of the system studied. According to the authors, the larger the value of the binding energy, the more easily an inhibitor could adsorb on the metal surface and the higher the inhibition efficiency. This observation is consistent with the result obtained for paucine in this study.

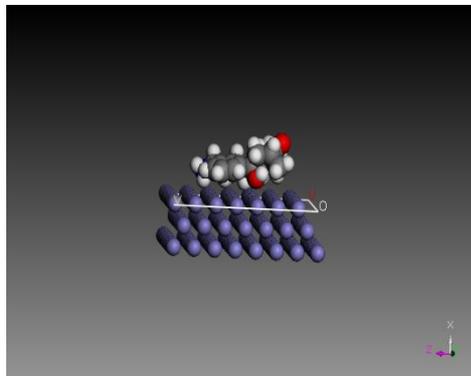


Figure 7: Molecular dynamics model of a single paucine molecule on Fe (110)

#### 4.0 Conclusions

1. PM extract was found to be an inhibitor for mild steel corrosion in 1 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub>.
2. The inhibition efficiency (IE%) of the extract increased with an increase in the concentration of PM extract and temperature and synergistically on addition of potassium iodide salt.
3. Calculated activation energies of adsorption were lower in the presence of PM extract indicating chemisorption.
4. DFT-based quantum-chemical computations of parameters associated with the electronic structures of the major active component of the extract confirmed the corrosion inhibiting potentials.
5. The present study provides new information on the inhibiting characteristics of PM extract under specified conditions. The environmentally friendly inhibitor could find possible applications in metal surface anodizing and surface coating in industries.

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