



Application of *Peperomia Pellucida* Leaves Extract as a Green Corrosion Inhibitor for Mild Steel in 1.0 M Hydrochloric Acid Solution

Odozi N.W., Saheed R. and *Mchihi M. M.

Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

*Correspondence Email: mosesmsenhemba@gmail.com

ABSTRACT

The inhibition efficiency of *Peperomia pellucida* (PP) leaves extract against the corrosion of mild steel in 1 M hydrochloric acid was investigated by weight loss and electrochemical methods. The inhibition efficiency (%I) decreased with increase in temperature. Results from weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) studies revealed that PP acted as a good inhibitor and inhibition efficiency reached 98.1 % at 1000 ppm inhibitor concentration. The values for Gibbs free energy ($\Delta G = -18.79$ kJ mol⁻¹ at 343 K) were negative, indicating that the adsorption of PP on the surface of mild steel is spontaneous. The values of ΔG also indicated that adsorption of PP on the mild steel surface was by physisorption and the generated data fitted the Langmuir adsorption isotherm. A decrease in entropy with increase in PP concentration was also observed. At 1000 ppm inhibitor concentration, $\Delta H = -32.58$ kJ mol⁻¹ was obtained. The negative value of ΔH indicated the exothermic nature of the corrosion process and adsorption of PP molecules on mild steel surface. Activation energy increased with a rise in PP concentration. Polarization studies revealed that PP acts as a mixed type inhibitor. Results of weight loss and electrochemical studies validate the use of *Peperomia pellucida* as inhibitor for corrosion of mild steel in acidic medium

Keywords: Corrosion, inhibition efficiency, inhibitor, mild steel, *Peperomia pellucida*

INTRODUCTION

Corrosion processes are responsible for numerous losses mainly in manufacturing industries. It is clear that the best way to combat it is prevention. Among the various methods ((such as use of corrosion inhibitors, material selection, coatings, cathodic protection, design) employed to prevent destruction or degradation of mild steel surface, the use of corrosion inhibitors is one of the best known methods of corrosion protection and one of the most useful in the industry. This method is receiving serious attention basically due to its simplicity, effectiveness, low cost and environmental friendliness (Fouda *et al.*, 2017).

The use of inorganic compounds (such as silicates, nitrates, phosphates, nitrites, and borates) and organic compounds (predominantly, those with O, N, S, and P hetero atoms) have been reported in literature as metal corrosion inhibitors in different corrosive environments (Fouda, *et al.*, 2014). The toxic effect of most of these compounds (i.e inorganic and organic corrosion inhibitors) on the environment has prompted the search for green corrosion inhibitors as they are biodegradable, inexpensive, readily accessible and renewable (Umoren *et al.*, 2011).

El-Hajjaji *et al.*, (2016) studied essential oil of thyme vulgaris as green corrosion inhibitor for mild steel in 1 M HCl and reported that *T. vulgaris* oil examined acted as an efficient

corrosion inhibitor in 1 M HCl. Corrosion inhibition and adsorption behaviour for aluminium by extract of *Aningeria robusta* in HCl solution was studied by Umoren *et al.*, (2011). *Aningeria robusta* extract was found to be an inhibitor for aluminium corrosion in HCl. *Peperomia pellucid* belongs to the family Piperaceae. It is a herbaceous plant found mainly in Africa, America and Asia used for treatment of abdominal pain, boils, rheumatic joint pain among other health challenges (Ngueguim *et al.*, 2017). This paper reports our findings on the corrosion inhibition efficiency of *Peperomia pellucid* on mild steel in 1 M HCl medium.

MATERIALS AND METHODS

Sampling, Extraction procedure and solution preparation

The PP leaves used for the study were obtained from Ibadan, Oyo state and were washed with distilled water and dried in an enclosed air conditioned research laboratory. The dried leaves were then pulverised to powder to increase the surface area for extraction. Soxhlet method of extraction and cold method were employed. 4 g of powder was used for extraction with 250 ml of solvent at 80°C for 8 h. Solvent used for the extraction was a mixture of ethanol, methanol and water in the ratio of 7:2:1. The solvents were later separated from the extract with the aid of rotary

evaporator at 40°C. 1 M HCl was prepared from 35.4% HCl using distilled water. The inhibitor test solutions were then prepared in the range of 100-1000 ppm, using 1 M HCl solution as solvent.

Weight loss measurements

Mild steel specimens used for this study were obtained commercially from an open market in Ibadan and mechanically press-cut into 4 × 4 cm dimensions. The coupons were washed thoroughly with distilled water and detergents and degreased with ethanol. The specimens were then rinsed with acetone, air-dried and weighed. Experiments were performed at 303 K, 313 K, 323 K, 333 K and 343 K with different concentrations of PP. The immersion time used for each temperature and concentration was 5 h. Experimental data were reported as mean values of triplicate analyses. The %I, CR and θ were calculated using the relationships presented in equation 1-3 (Ekemini *et al.*, 2017).

$$CR = \frac{(W_o - W_1)}{A t} \quad (1)$$

$$\%I = \left(\frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right) \times 100 \quad (2)$$

$$\%I = \theta \times 100 \quad (3)$$

Where W_o = weight of coupon before immersion, W_1 = weight of coupon after immersion, A = area, t = immersion time, θ = surface coverage, CR_{blank} = corrosion rate for mild steel in the blank and CR_{inh} = corrosion rate for mild steel in the PP inhibited solution.

Electrochemical Tests

The usual three electrode set up comprising of saturated calomel electrode (SCE) as reference electrode, platinum as counter electrode and the mild steel as working electrode was used. A Princeton Applied Electrochemical Workstation was used for all electrochemical tests. The system was allowed to attain steady open circuit potential (OCP) between 0 and 1800 s before measurements were made (El-Bindary *et al.*, 2015). EIS was conducted at frequency of 10 kHz to 10 mHz at room temperature. Polarization measurements were

conducted between -0.15 V to +0.15 V vs. E_{OC} at scan rate of 0.2 mV/s. Experiments were performed in 1 M HCl without and with 100 ppm, 500 ppm and 1000 ppm of PP. The data generated were analyzed by means of Nyquist and Tafel plots. Values of charge transfer resistances obtained were used to compute the inhibition efficiency according to Eq. 4. Double layer capacitance (C_{dl}) of the adsorbed film was computed from constant phase element (CPE) constant (Y_o) and charge transfer resistance (R_{ct}) using Eq. 5. Corrosion current densities were obtained from analyses of Tafel plots and used to also calculate inhibition according to Eq. 6 (El-Hajjaji *et al.*, 2016 & Chaouiki *et al.*, 2018).

$$\mathcal{E}_{EIS} = 100 \left(\frac{R_{ctI} - R_{ctB}}{R_{ctI}} \right) \quad (4)$$

$$C_{dl} = (Y_o R_{ct}^{n-1})^{\frac{1}{n}} \quad (5)$$

$$\mathcal{E}_{PDP} = 100 \left(1 - \frac{I_{corr}^i}{I_{corr}^b} \right) \quad (6)$$

where R_{ctB} and R_{ctI} = charge transfer resistances in the absence and presence of PP respectively, I_{corr}^b and I_{corr}^i = the corrosion current densities in the absence and presence of the PP respectively, n is a constant showing degree of roughness of the metal surface obtained from the phase angle given that ($j^2 = -1$) α and $n = 2\alpha(\pi)$ (El-Hajjaji *et al.*, 2016).

RESULTS AND DISCUSSION

Weight loss

The %I and θ of PP against the corrosion of mild steel in free 1 M HCl and inhibited test solutions are presented in Table 1. It can be clearly seen that %I increased considerably as PP concentration increased. This may be as a result of increased number of PP molecules adsorbed on the mild steel surface thus providing wide surface coverage (Loto *et al.*, 2013). However, as the temperature increases, the CR increases and %I decreases. The highest %I (98.1 %) was observed when the corrosive medium was treated with 1000 ppm of PP.

Table 1: Percentage inhibition and surface coverage for mild steel corrosion in free 1.0 M HCl and PP inhibited test solutions obtained from weight loss measurements.

Temperature (K)		100 ppm	300 ppm	500 ppm	800 ppm	1000 ppm
303	%I	89.50	91.2	92.4	95.3	98.1
	θ	0.895	0.912	0.924	0.953	0.981
313	%I	84.2	86.3	88.6	94.0	97.9
	θ	0.842	0.863	0.886	0.940	0.979
323	%I	73.8	81.7	85.4	93.2	97.7
	θ	0.738	0.817	0.854	0.932	0.977
333	%I	71.6	72.5	82.9	85.7	88.0
	θ	0.716	0.725	0.829	0.857	0.880
343	%I	70.8	71.9	80.0	81.6	84.2
	θ	0.780	0.719	0.800	0.816	0.842

Adsorption isotherm and thermodynamic analysis

High linearity was observed ($R^2 = 0.89858$ to 0.99856) by plotting C/θ Vs C according to equation 7 shown in Figure 1, which indicated that the adsorption of this compound obeyed Langmuir isotherm (Kandri Rodi *et al.*, 2016). The negative value of ΔG_{ads} computed with the aid of equation 10 indicates that the adsorption of PP molecules on the mild steel surface is spontaneous (Mahendra *et al.*, 2015). The range of

values of ΔG_{ads} obtained for this study portrayed physisorption.

$$\frac{C}{\theta} = C + \frac{1}{K_{\text{ads}}} \quad (7)$$

ΔH and ΔS were determined using the transition state equation (equation 8) by making a plot of $\log(CR/T)$ against $1/T$ (Figure 2). The negative values of ΔH reflect the exothermic nature of the process.

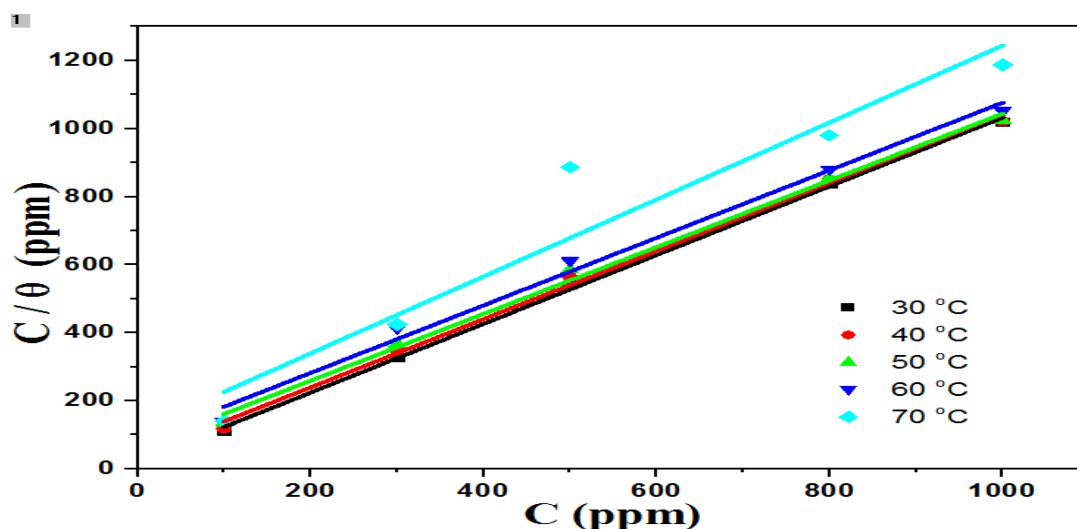


Figure 1. Langmuir plots for mild steel corrosion in free 1 M HCl and PP inhibited test solutions

Table 2. Parameters computed from Langmuir plots for mild steel corrosion in free 1.0 M HCl and PP inhibited test solutions

Temperature (K)	R^2	K_{ads}	ΔG_{ads} (kJ mol ⁻¹)
303	0.99856	2.22	-12.12
313	0.99612	5.37	-14.82
323	0.99419	7.54	-16.21
333	0.98867	12.78	-18.19
343	0.89858	13.08	-18.79

Table 3. Thermodynamic parameters for mild steel corrosion in free 1 M HCl and PP inhibited test solutions

Solution(ppm)	Ea (kJ/mol)	Δ H (kJ/mol)	ΔS (kJ/mol K)
Blank	45.5	-14.26	0.22
100	66.1	-22.63	0.20
300	69.1	-26.50	0.19
500	63.5	-27.39	0.18
800	74.4	-32.21	0.18
1000	94.81	-32.58	0.17

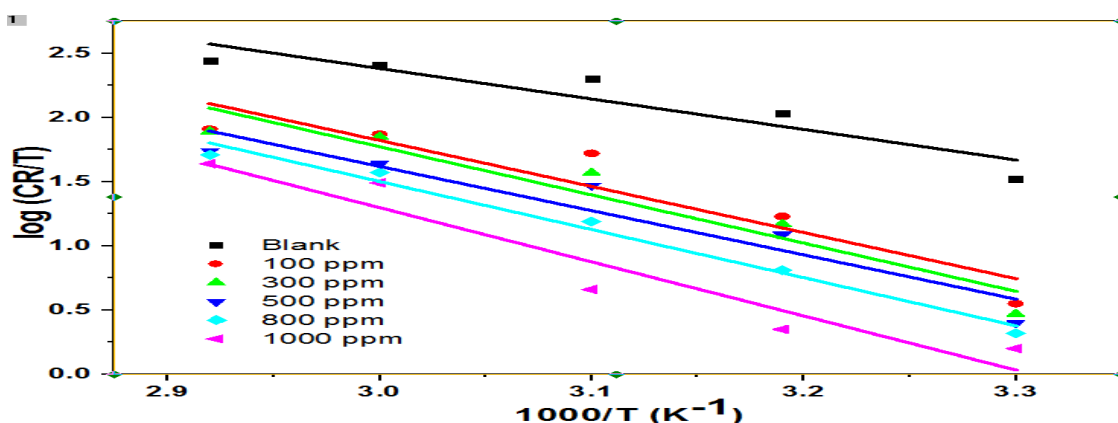


Figure 2. Transition state plots for mild steel corrosion in free 1.0 M HCl and PP inhibited test solutions

Activation energy (Ea) of the corrosion of mild steel

The activation energy plays a vital function in understanding the mechanism of inhibition of the inhibitors. Ea was computed using equation 9 by making a plot of logarithm of corrosion rate (log CR) versus 1/T (Figure 3). Ea (determined using the Arrhenius plot) increased on addition of PP compared to Ea obtained for the uninhibited solution which implies that PP actually increased the energy barrier that molecules of HCl must overcome in order to corrode the mild steel. The range of Ea values (from 45.5 kJ/mol to 74.4 kJ/ mol) is lower than the threshold value of 80 kJ/mol required for chemical adsorption

(Manimegalai and Manjula, 2015). This suggests that the adsorption of PP on mild steel is due electrostatic interaction between the charged molecules and charged steel surface (physisorption).

$$CR = \frac{RT}{N_h} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \tag{8}$$

$$\log CR = -\frac{E_a}{2.303RT} + \log A \tag{9}$$

$$\Delta G_{ads} = -RT \ln (55.5 \times K_{ads}) \tag{10}$$

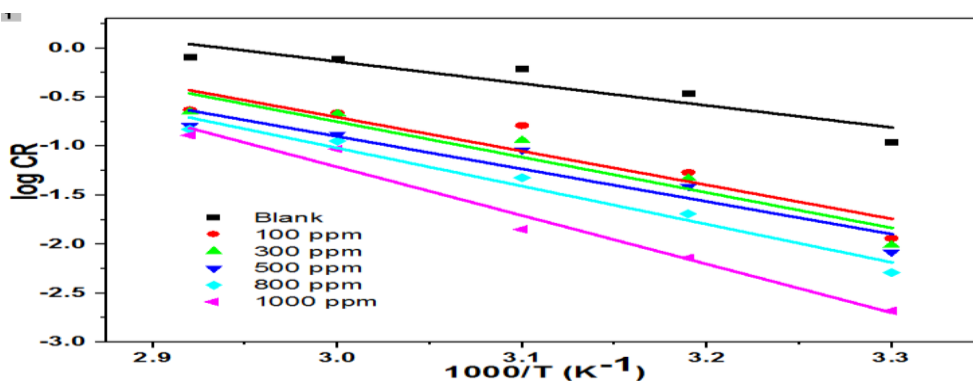


Figure 3. Arrhenius plots for mild steel corrosion in free 1.0 M HCl and PP inhibited test solutions

Electrochemical impedance spectroscopy (EIS)

Nyquist plots obtained for mild steel in 1.0 M HCl in the absence and presence of different concentrations of PP is presented in Figure 4 and the parameters determined from EIS analysis are presented in Table 4. It is noticeable from the nyquist plots that the diameter of capacitive loop considerably changed after addition of PP and the maximum effect was observed at 1000 ppm. In addition, these impedance diagrams are not perfect semicircles and this difference has been attributed to frequency dispersion. However, the PP addition is found to boost R_{ct} values and lower C_{dl} values (Saqalli *et al.*, 2017). The decrease in C_{dl} may be due to the adsorption of PP on mild steel surface leading to the development of film resulting to

decrease in the rate of corrosion (KandriRodi *et al.*, 2016).

Potentiodynamic Polarization Measurements

The effect of PP concentration on the anodic and cathodic polarization behavior of mild steel in 1M HCl solution has been studied by polarization measurements and the recorded. Tafel plots for some studied concentrations are shown in Figure 5. The respective electrochemical parameters derived from the plots including corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a and β_c respectively) and inhibition efficiency, $\epsilon_{PDP}(\%)$ are presented in Table 5.

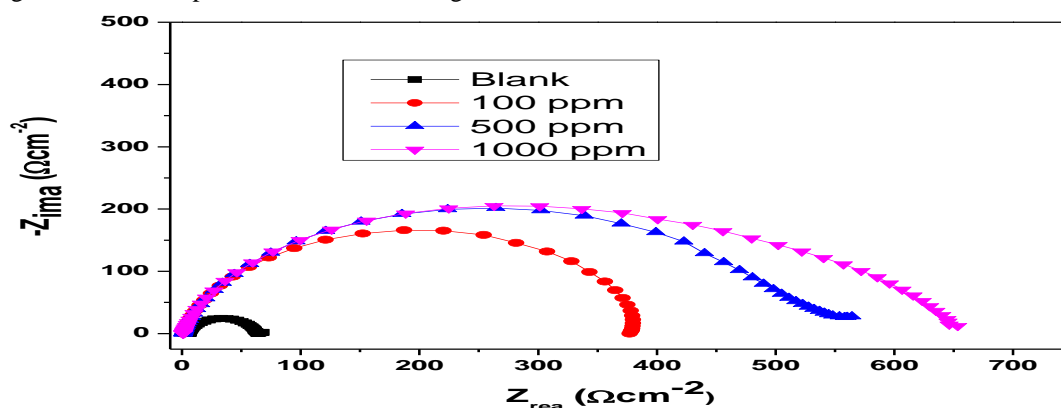


Figure 4. Nyquist plots for mild steel corrosion in free 1.0 M HCl and PP inhibited test solutions.

The results in Table 5 showed that the I_{corr} decreased noticeably after the addition of PP. In the presence of PP E_{corr} boosted with no definite trend, indicating that PP act as mixed-type

inhibitors. The inhibition efficiency was computed according to equation 6 and $\epsilon_{PDP}(\%)$ increases with a rise in PP concentration.

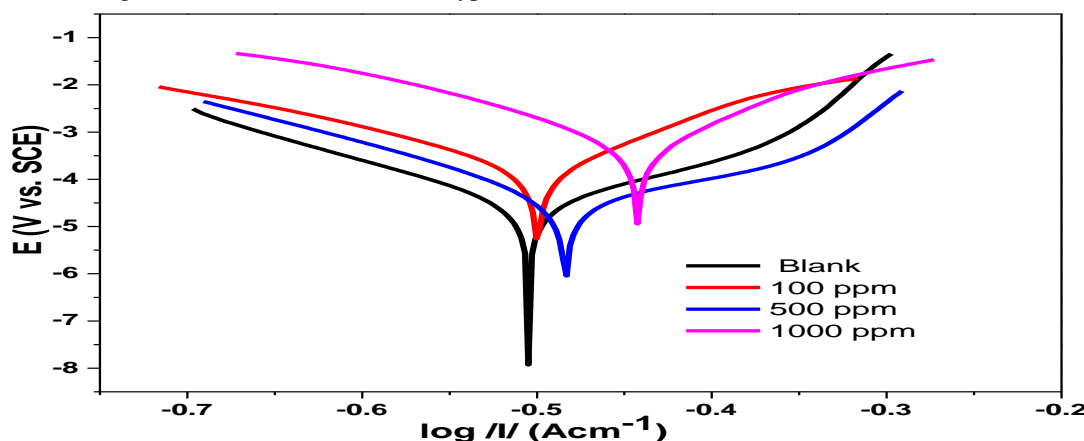


Figure 5. Tafel plots for mild steel corrosion in free 1.0 M HCl and PP inhibited test solutions

Table 4. EIS Parameters for Mild Steel Corrosion in free 1.0 M HCl and PP Inhibited Test Solutions

	R_s (Ωcm^2)	R_{ct} ($\Omega\text{ cm}^2$)	N	Y_o ($\mu\Omega^{-1}\text{s}^n\text{cm}^{-2}$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	%I
Blank	0.983	56.2	0.886	155.8	14.2	-
100 ppm	1.102	389.5	0.871	101.6	9.1	85.6
500 ppm	1.206	602.4	0.814	90.4	3.8	90.7
1000 ppm	1.312	695.5	0.808	62.1	0.4	91.9

Table 5. PDP parameters for mild steel corrosion in free 1 M HCl and PP inhibited test solutions

System	β_a (mVdec ⁻¹)	β_c (mVdec ⁻¹)	I_{corr} (μ Acm ⁻²)	E_{corr} (mV/SCE)	ϵ_{PDP} (%)
Blank	66.8	84.5	951.1	-498	
100 ppm	76.3	91.35	128.9	-481	86.4
500 ppm	77.5	97.8	99.8	-483	89.5
1000 ppm	94.2	102.2	76.3	-480	92.0

CONCLUSION

The study showed that PP exhibited good performance as a corrosion inhibitor for mild steel corrosion in 1.0 M HCl. Polarization measurement revealed that PP behaved as a mixed kind of inhibitor for mild steel corrosion in 1.0 M HCl. EIS analysis revealed that the addition of PP enhanced R_{ct} values and lowered C_{dl} values. The adsorption of PP on mild steel obeyed Langmuir adsorption isotherm.

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