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Pouteria Campechiana As A Green Corrosion Inhibitor for Mild Steel in HCl Solution

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Abstract

The corrosion inhibition behaviour of *Pouteria campechiana* (PC) leaves on mild steel in 1M HCl medium was investigated by gravimetric, polarization, electrochemical impedance measurements and temperature studies. The inhibition efficiency was found to increase with increasing concentration of the extract. Adsorption of extract molecules on mild steel surface obeyed the Langmuir and Temkin adsorption isotherms. The results obtained prove that the leaves of *Pouteria campechiana* act as a good corrosion inhibitor.

Keywords
Mild steel, acid corrosion, *Pouteria campechiana*, HCl medium, Potentiodynamic polarisation.

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1. INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors is one of them [1]. Corrosion phenomena, control and prevention are unavoidable major scientific issues that must be addressed daily as far as there are increasing needs of metallic materials in all facets of technological development [2]. The effects of corrosion on metals are more than just loss of metal; according to [3], corrosion affects the safe, reliable, and efficient operation of equipment or structures. The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is one of the acceptable practices of reducing and/or preventing corrosion [4]. When small concentrations are added to corrosive media, they either decrease or prevent the reaction of the metal with the media. Inhibitor hinders corrosion reactions either by reducing the probability of corrosion occurrence or by reducing the rate of attack or by both [5]. Though many synthetic compounds have shown good anticorrosive activity, most of them are highly toxic to both human beings and environment [6]. Organic substances (plant based) containing functional groups with oxygen, nitrogen and /or sulphur atoms in a conjugate system have been reported to exhibit good inhibiting properties. The polar functional groups are usually regarded as the reaction center for the establishment of the adsorption process [7]. Natural products have been studied extensively as corrosion inhibitors both in product mixtures extracted from natural sources such as plants or essentially pure products derived from animals or plants (i.e. vitamins and amino acids). In the last years, Umoren and Obot's research group evaluated plant extracts as CIs, for example, Phyllanthus amarus[8], Pachylobus edulis [9-10] Raphia hookeri [11-12] and Ipomoea involcrata, [13] and also described the inhibitive action of ethanolic extracts from leaves of Chlomolaena Odorata L. (LECO) as eco-friendly CI of acid corrosion of aluminum in 2 M HCl, using hydrogen evolution and thermometric techniques[14].

In general, the plant extracts are inhibitors with high inhibition efficiency and are non-toxicant. Anbarasi et al., have studied mild steel corrosion inhibition by Cucurbita maxima plant extract in hydrochloric acid solution [15]. Oloruntoba and Toyin have investigated water hyacinth (Eichhornia crassipes) leaves extract as CI for AISI 1030 steel in sea water [16]. Akalezi et al. [17] have found the inhibitive effect of the aqueous extract of *Coffee senna* (CS) on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions. Srivastava and Sanyal have studied the performance of caffeine and nicotine in the inhibition of steel corrosion in neutral media [18]. Plant extracts have become important as environmentally acceptable, readily available and renewable source for wide range of inhibitors [5]. The present study focused on using *Pouteria campechiana* leaves (Scheme 1) extract as inhibitor to prevent corrosion since it is economically viable, nontoxic, ecologically friendly and causes little or no threat to the environment.

2. EXPERIMENTAL

2.1 Collection and extraction of plant material

Green leaves of plant *Pouteria campechiana* were collected and authenticated by Dr. John Britto, The Rapient Herbarium and Centre for Moduler Systematics, St.Joseph's college, Trichirappallli, Tamilnadu, India. *Pouteria campechiana* powder (10g) was boiled with 100 ml double distilled water and condensed to 50 ml. The extract was left to cool down and then filtered using Whatman filter paper. From that various concentrations were prepared [19].

Figure 1: ***Pouteria campechiana***

2.2 Specimen preparation

Mild steel specimens with the composition Carbon = 0.07%; Sulphur = 0%; Phosphorus = 0.008%; Silicon = 0%; Manganese = 0.34% and Iron = Reminder and size of 4 × 1 × 0.1 cm were used for weight loss, same composition embedded in polytetrafluoroethylene (PTFE) with exposed measurements. The electrode was polished using a sequence of emery papers and the thickness of mild steel specimens and the radius of the holed were determined with the help of Vernier Caliper of high precision and the surface areas of the specimens were calculated.

2.3 Determination of inhibition efficiency

Weight loss measurements were done according to the method described previously [20-22]. Weight loss measurements were performed at 303 ± 1K for 2h by immersing the mild steel specimens in 1M HCl solutions (100 mL) without and with various concentrations of inhibitor (0.2%-1.0%) concentrations respectively. After the elapsed time, the specimen was taken out, washed, dried, and weighed accurately. All the concentrations of the inhibitor for weight loss and electrochemical study were taken in percentage concentration (%).

Corrosion Rate (mpy) = $87.6 \times W/ADT$ --- (1)

W= Weight loss in mg, A=Area of the mild steel sample in cm^2, D=Density of the mild steel g/cm^3; T= Exposure time in hrs.

The surface coverage (θ) and inhibition efficiency (IE %) were determined by following equations.

$\theta = W_0 - W_1/W_0$ --- (2)

$I.E (\%) = W_0 - W_1/W_0 * 100$ --- (3)

Where, W_1 and W_0 are the weight loss values in g in presence and absence of inhibitors, respectively.

2.3.1 Weight loss method at different temperatures

The loss in weight was calculated at different temperatures from 303K to 333K. Each experiment was duplicated to get good reproducibility. Weight loss measurements were performed in 1M HCl with and without the addition of the inhibitor at their best inhibiting concentration (1.0%). Percentage inhibition of the inhibitor at various temperatures was calculated.

2.3.2 Potentiodynamic polarisation measurements

Potentiodynamic polarisation studies have been performed for mild steel specimen both in the presence and the absence of the inhibitors.

Potentiostatic polarization studies were carried out using a CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm^2 area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. Polarization curves were recorded using IR compensation. The results, such as Tafel slopes, and I_{corr}, E_{corr} and LPR values were calculated. During the polarization study, the scan rate (v/s) was 0.01; hold time at E_f (s) was zero and quit time(s) was 2.

2.3.3 AC-Electrochemical impedance spectroscopy

A CHI electrochemical impedance analyzer (model 660A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to attain its open circuit potential. The real part Z' and imaginary part Z" of the cell impedance were measured in ohms at various frequencies. The values of the charge transfer resistance R_t, double layer capacitance C_{dl} and impedance value were calculated.

$R_t = (R_s + R_t) – R_s$ ------------- (3)

Where R_s = solution resistance

$C_{dl} = ½ \pi R_t f_{max}$ -------------- (4)

Where f_{max} = maximum frequency AC impedance spectra were recorded with initial E (v) = 0; high frequency (Hz) = 1; amplitude (v) = 0.05; and quiet time(s) = 2.

RESULTS AND DISCUSSION

3.1 Weight Loss measurements:

The weight loss studies for the various concentrations of *Pouteria campechiana* leaves extract have been carried out in the concentration range 0.2% to 1.0% at 303 ± 1K in 1M HCl to understand the influence of various concentrations of PC extract on the corrosion inhibition of mild steel for a period of 2 hours. The corrosion parameter obtained from weight loss measurements for mild steel in 1M HCl solution containing various concentrations of PC extract are shown in Table-1. It was found that the increase in the concentration of the CP extract, the corrosion rate was decreased, and the inhibition efficiency increased from 53.84 to 76.92%. These results indicated that the best inhibiting concentration was obtained at 1.0% concentration. The effect of inhibition efficiency with various concentrations of CP extract on mild steel in 1M HCl is shown in table-1[23].

Table-1 Corrosion rate, inhibition efficiency and surface coverage of mild steel immersed in 1 M HCl for various concentrations of PC obtained by weight loss method at 303 ± 1K

S. No.	Concentration of inhibitor (v/v %)	Corrosion Rate (mpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
1.	Blank	54.33	-	-
2.	0.2	25.07	53.84	0.5384
3.	0.4	23.68	56.41	0.5641
4.	0.6	20.89	61.53	0.6153
5.	0.8	16.71	69.23	0.6923
6.	1.0	12.53	76.92	0.7692

The effect of temperature on the performance of PC extract clearly indicated that the inhibition efficiency decreases with increase in temperature. We know that the adsorption and desorption of inhibitor molecules continuously occur at the metal surface and equilibrium exists between two processes at a particular temperature. But, with the increase of temperature, the equilibrium between adsorption and the desorption processes is shifted to a higher desorption. It explains the lower inhibition efficiency at higher temperature. Decrease in performance of compounds with increase in temperature is due to the weakening of bonds between metal surface and the inhibitors.

The effect of temperature on the rate of corrosion process was studied in different temperatures ranging from 303K to 333K (30°C to 60°C) at their best protecting concentration on 1.0%. The extract of PC is able to maintain an inhibition of about 72.88% up to 313 K and the inhibition is found to decline to 66.66% at 333 K in 1M HCl medium and the results are presented in Table - 2.

Table-2 Values of corrosion rate, inhibition efficiency and surface coverage for different temperatures in the presence of 1.0% concentration of PC in 1M HCl.

S. No.	Temperature (K)	Corrosion Rate (mpy)	Inhibition efficiency (%)	Surface coverage (θ)
1.	303	12.53	76.92	0.7692
2.	313	44.58	72.88	0.7288
3.	323	55.72	68.99	0.6899
4.	333	68.26	66.66	0.6666

3.2 Adsorption Isotherm:

Basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. The degree of surface coverage (θ) for different concentrations of inhibitors in 1M HCl has been evaluated using weight loss. The data were graphically fit to Temkin's isotherms. Figure - 2 shows the plot of surface coverage (θ) versus 2+logC and the expected linear relationship is obtained for PC in 1M HCl. The strong correlation (R^2= 0.965 for PC in 1M HCl) is obtained which confirms the validity approach.

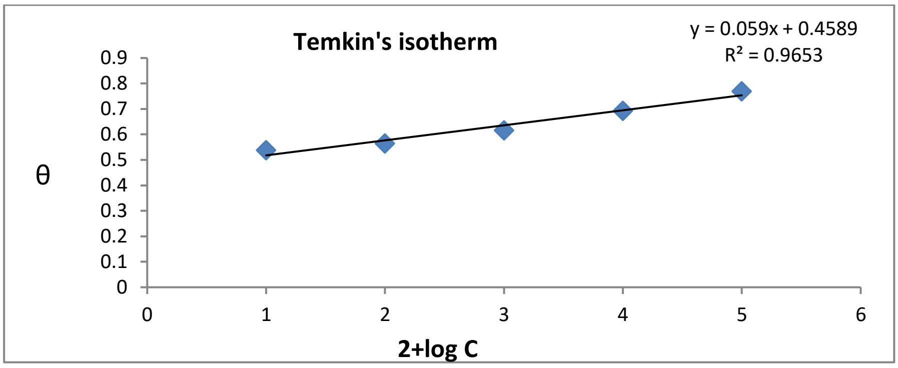

Figure 2: Temkin's adsorption isotherm for mild steel in 1M HCl in the presence of PC at different concentrations.

The use of adsorption isotherm provides useful insight into the corrosion inhibition mechanism. Figure - 3 shows the plot of C/θ versus 2+logC and the expected linear relationship is obtained for PC in 1M HCl suggesting that the adsorption of PC extract on the surface of mild steel in 1M HCl solution follows Langmuir adsorption isotherm [24-26].

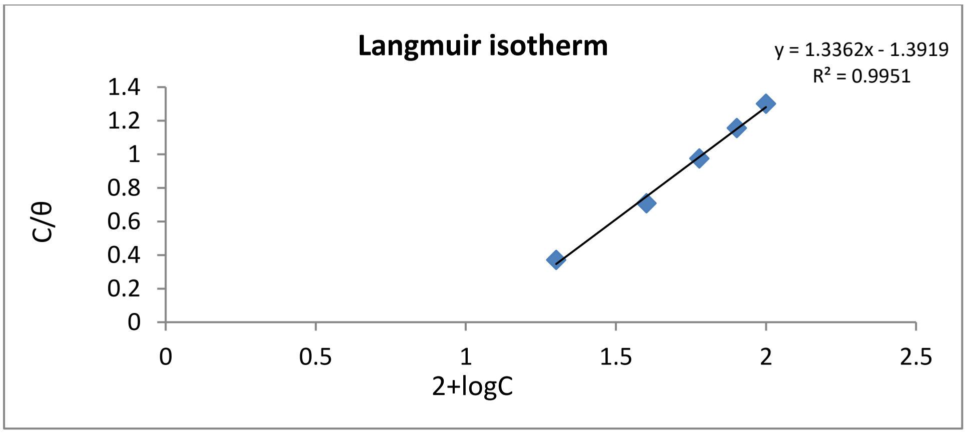

Figure 3: Langmuir adsorption isotherm for mild steel in 1M HCl in the presence of PC at different concentrations.

3.3 Potentiodynamic polarisation measurements

Electrochemical corrosion kinetic parameters such as corrosion potential potential (E_{corr}), corrosion current (I_{corr}), anodic and cathodic tafel slopes (b_a and b_c) and percentage of IE for the corrosion of mild steel in 1M HCl at 30°C in the absence and presence of different concentrations of the inhibitor are given in Table - 3 and its corresponding polarisation curves are shown in Figure - 4. It is seen from the tables that the corrosion current density (I_{corr}) markedly decreased with the addition of the inhibitor and corrosion potential shifts to less negative values upon addition of the inhibitor. Moreover, the values of anodic and cathodic Tafel slopes (b_a and b_c) are slightly changed indicating that this behaviour reflects the acid dissolution of the inhibitor ability to inhibit the corrosion of mild steel in 1M HCl via adsorption of its molecules on both anodic and cathodic sites and consequently, it act through mixed mode of inhibition [27-32].

Table - 3 Potentiodynamic polarization measurements for the corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of PC

S. No	Concentration v/v%	$-E_{corr,}$ mV vs SCE	$I_{corr,}$ A/cm^2	$b_{c,}$ mV/decade	$b_{a,}$ mV/decade	LPR Ohm cm^2	% I.E
1.	Blank	0.471	6.058×10^{-4}	0.1447	0.1040	43.5	-
2.	0.2	0.474	2.730×10^{-4}	0.1362	0.0800	80.1	54.93
3.	1.0	0.463	1.615×10^{-4}	0.1179	0.0870	135.0	73.34

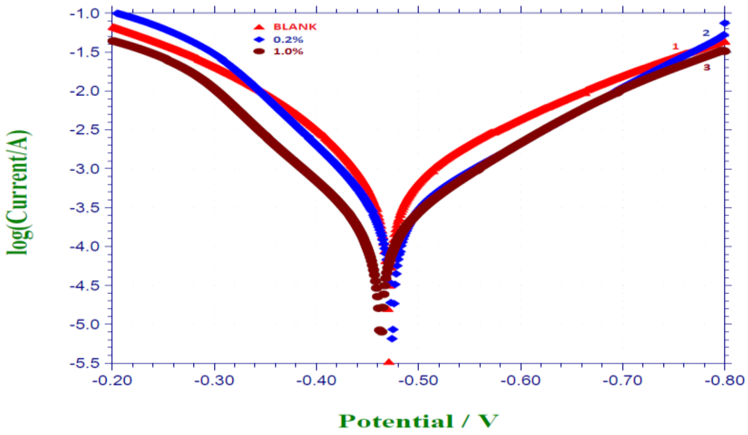

Figure 4: Potentiodynamic polarization curve for mild steel in 1M HCl in the absence and presence of various concentrations of PC.

3.4 AC-Electrochemical impedance spectroscopy

Impedance spectra (Nyquist plots) of mild steel in 1M HCl containing various concentrations of the inhibitor at 30°C are shown in Figure - 5. It is apparent from the plots that the impedance of the inhibited solution has increased with an increase in the concentration of the inhibitor. The experimental results of EIS measurements for the corrosion of mild steel in 1M HCl in the absence and presence of the inhibitor are given in Table - 4. It can be concluded that the charge transfer resistance (R_{ct}) value increased with an increase in the concentration of the inhibitor, whereas values of the double-layer capacitance (C_{dl}) of the interface start decreasing, with an increase in the inhibitor concentration, which is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer [33-35].

Table - 4 Impedance measurements for the corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of PC

S. No.	Concentration (v/v %)	R_{ct} (ohm cm^2)	C_{dl} (F/cm^2)	Imp (log z/ohm)	P.A	% I.E
1.	Blank	2.280	7.22×10^{-7}	0.5820	23.29	-
2.	0.2	5.059	3.25×10^{-7}	0.9050	45.92	54.99
3.	1.0	7.430	2.21×10^{-7}	1.3300	66.42	69.39

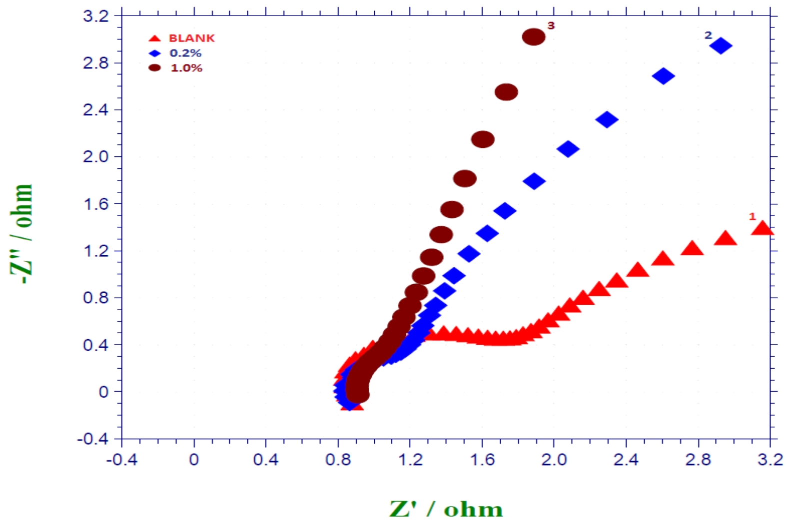

Figure 5: Impedance diagram for mild steel in 1M HCl in the absence and presence of various concentrations of PC.

4. CONCLUSIONS

The *Pouteria campechiana* leaves extract has good inhibition efficiency for preventing the corrosion of mild steel in 1 M hydrochloric acidic medium. *Pouteria campechiana LE* extract formed a protective layer on the surface of the mild steel and improved surface condition, due to adsorption, for the corrosion protection. The values obtained from the weight loss technique for the studied inhibitor fit into the Langmuir and Temkin adsorption isotherms. The corrosion process was inhibited by adsorption of the active components on the mild steel surface.

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