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Extract of *Phyllanthus fraternus* Leaves as Corrosion Inhibitor for Mild Steel in H_2SO_4 Solutions

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The inhibitive action of extract of Phyllanthus fraternus leaves as corrosion inhibitor for mild steel in H_2SO_4 solutions was investigated using conventional weight loss, gasometric techniques, electrochemical polarizations and electrochemical impedance spectroscopy. The results showed that the extract of Phyllanthus fraternus leaves performed well as inhibitor for the corrosion of steel in sulphuric acid media. Inhibition efficiencies increased with increasing concentration of the plant extract but decreased with the temperature rise. Both the cathodic hydrogen evolution and the anodic dissolution of mild steel was inhibited, hence the active molecule of the extract studied acted as a mixed type corrosion inhibitor.

Keywords: Phyllanthus fraternus; corrosion inhibition; electrochemical polarization; electrochemical impedance spectroscopy; mild steel.

1. INTRODUCTION

The amount of sulphuric acid used in the chemical industry for removal of the undesired scales and rust is enormous. The addition of corrosion inhibitors effectively secures the metal against these severe acid attacks. Many studies in this regard using organic inhibitors have been reported [1-4]. Most of the inhibitors are organic compounds with N, S and O hetero-atoms have higher electron density making them the reaction centers. These compounds are adsorbed on the metallic surface and block the active corrosion sites and most of them are highly toxic to both human beings and environment [5-7]. Hence use of the natural products as eco-friendly and harmless corrosion inhibitors, has become popular [8-17]. This kind of inhibitors was used as extract or oil and may play a major role in protecting metals from attack in pickling and/or bath acid solutions.

In this optic, we have selected *Phyllanthus fraternus* which is Euphorbiaceous family plant and perhaps originated from western parts of India. There are reports available on phytochemical analysis of leaves extract of *Phyllanthus fraternus*. Among the wide use of the aqueous extract of *Phyllanthus fraternus*, we may cite as examples the protective effect against bromobenzene induced mitochondrial dysfunction in rat liver mitochondria. The plant extract contains alkaloids like morphine and boldine [18] and its antinociceptive activity of PF in chronic inflammatory hyperalgesia and also indicates that it might be potentially effective in management of the persistent pain [19]. Extract also contains tannins, saponin, terpenoid and steroid [20]. the present work was then aimed to test the aqueous extract of *Phyllanthus fraternus* against a mild steel in H_2SO_4 solutions. The study was conducted using weight loss, gasometric techniques, electrochemical polarizations and electrochemical impedance spectroscopy.

2. EXPERIMENTAL

2.1. Preparation of Herbal Extracts Solutions

About 25 g of dried and powdered leaves of *Phyllanthus fraternus*was refluxed with 1 M H_2SO_4 for about 5 h and was kept overnight to completely extract the basic components as these are soluble in the acid. The solution was filtered off and the filtrate was diluted to 500 ml with 1 M H_2SO_4 prepared as above. To know the concentration of mass of plant compounds extracted, 100 ml of the extract was taken to neutralize with 1 M NaOH up to pH 8 in order to liberate the solid base from the salt formed in the extract. The neutralized solution was then extracted with chloroform. The chloroform layer consisting of basic organic compounds was evaporated and the resultant gummy material obtained was dried and powdered and weighed accurately by digital micro-balance. From the stock solution, concentrations of 0.5, 1.0, 2.0, 3.0 and 4.0 g/l were prepared.

2.2. Preparation of Electrodes

As described above three types of electrodes were used in the study. To prepare WE, mild steel (MS) rod sample **(**0.09% P, 0.37% Si, 0.01% Al, 0.05% Mn, 0.19% C, 0.06% S and the remainder Fe**)**was obtained and carefully cut into many cylindrical electrodes.The upper area of the WE was then precisely covered with the Teflon and epoxy coating. The area of exposed surface of WE was measured precisely, with Vernier caliper.For the weight loss methodspecimens used (length = 2 cm, width = 2 cm, thickness = 0.1 cm) with a tiny hole on the upper part of it.This prepared WE was washed with a luke warm mild detergent (Surf) solution to remove greasy materials and then cleaned and washed repeatedly with double distilled water.It was quickly dried with a soft tissue paper and air dried then shifted into a desiccator or into the electrolyte in polarization cell.

2.3. Phytochemical Screening

Phytochemical screening was carried out on the extracts from *Phyllanthus fraternus*by previously described method. The plant extracts were screened for alkaloids, saponins, tannins, flavonoids, glycosides, terpenoids, steroids and phenobutinon.

2.4. Weight Loss and Gasometric Method

The polished and pre-weighed MS specimens were tied with threads and suspended in 100 ml test solutions, 1.0 M $H_2SO_4$with and without the inhibitor of different concentrations, for 2h of immersion at temperatures of 30^{o}C, 40^{o}C and 50^{o}C.The temperature was controlled by an aqueous thermostat.After the immersion test, the specimens were carefully washed in double-distilled water, dried and then weighed.The rinse removed loose segments of the film of the corroded samples.Duplicate experiments were performed in each set of the test and the mean value of the WL is reported.The loss in weight was determined by analytic digital micro-balance.

For the gasometric technique, high corrodent concentration is required; hence 5.0 M H_2SO_4 is used. In this technique, corrosion reactions in aqueous media are characterized by the evolution of gas resulting from the cathodic reaction, which is proportional to the rate of corrosion. The rate of evolution of the gas (R_H) is determined from the slope of the graph of volume of gas evolved (V) versus time (t).

$$\theta = \frac{R_{H0} - R_{Hi}}{R_{H0}} \quad (1)$$

$$\eta = \frac{R_{H0} - R_{Hi}}{R_{H0}} \times 100 \quad (2)$$

where R_{H0} and R_{Hi} are the rates of hydrogen evolution in the absence and presence of the plant extracts, respectively.

2.5. Electrochemical and Impedance Measurements

The AC impedance measurements are shown as Nyquist plots and polarization data as Tafel plots. The Electrochemical Analyzer Workstation (Autolab – PGSTAT 302N) was employed for this purpose. Polarization curves were obtained with a scan rate of 0.01 V/s in the range of ± 10 mV for LPR and ± 250 mV for TI vs. the E_{corr} of the WE of the MS and measured against the SCE.Impedance measurements were carried out at the constant value of E_{corr} after the electrode had been immersed60 minutes in the test solution. The frequency range applied was 0.1Hz to 1000Hz.The A.C. signal was 5 mV peak-to-peak with 12 data points per decade.

3. RESULTS AND DISCUSSION

3.1. Weight Loss Measurements

Based on the WL measurements, W_{corr} and the E_w%for various concentrations of *Phyllanthus fraternus* leaves extract, after 2 h of immersion at the temperatures of 30°C, 40°C and 50°C are given in Table-1. The following equation was used to determine the inhibition efficiency (E_w%):

$$E_W\% = 100 \times \frac{W_0 - W_{corr}}{W_0} \quad (3)$$

Where$W_{corr}$and W_0 are the corrosion ratesof steel with and without the additive, respectively.

From the Table-1, it could be observed that the values of E_w %were gradually increased with the increase in concentration of *Phyllanthus fraternus* leaves extract, reaching a maximum value of 85.80 % at the highest concentration of 4.0 g/l at temperature of 30°C.With increase in temperature from 30°C, 40°C and 50°C, there was a slight decrease in the value of E_w% which may be attributed to the negligible removal of loosely adsorbed some additive molecules by mechanical vibration of thermal energy.

Table 1. Inhibition Efficiency of MS in 1 M H_2SO_4 at various temperatures in the presence and absence of different concentrations of *Phyllanthus fraternus* leaves extract

Temperature (°C)	Concentration g/liter	W (μg/cm² h)	Inhibition Efficiency IE (%)	θ
30	1 M H_2SO_4	17.25	-	-
	0.5	5.56	67.77	0. 6777
	1.0	4.90	71.59	0. 7159
	2.0	4.08	76.35	0. 7635
	3.0	3.36	80.52	0. 8052
	4.0	2.45	85.80	0. 8580
40	1 M H_2SO_4	18.26	-	-
	0.5	6.68	63.42	0. 6342
	1.0	5.90	67.69	0. 6769
	2.0	4.83	73.55	0. 7355
	3.0	3.98	78.20	0. 7820
	4.0	3.26	82.15	0. 8215
50	1 M H_2SO_4	19.48	-	-
	0.5	8.01	58.88	0. 5888
	1.0	7.18	63.14	0. 6314
	2.0	6.35	67.40	0. 6740
	3.0	5.65	70.80	0. 7080
	4.0	4.78	75.46	0. 7546

The degree of surface coverage θ at different concentrations of the additive in acidic media has been evaluated from WL using the equation:

$$\theta = \frac{W_0 - W_{corr}}{W_0} \quad (4)$$

From Table-1, it could be observed that the increase in the value of $W_0$was more pronounced with the rise in temperature for the blank acid solution. In the presence of *Phyllanthus fraternus* leaves extract, the value of θ was decreased slightly when experimental temperature was increased, which could be caused by desorption of the extract molecules from the MS surface.

3.2. Gasometric Measurements

The volume of hydrogen evolved during the corrosion of MS in 5.0 M H_2SO_4 solutions in the absence and presence of *Phyllanthus fraternus* leaves extract was studied and the rates of hydrogen evolution was obtained. The rate of hydrogen evolution values are given in Table 2 and the difference of rate of hydrogen evolved for the different extract concentration are shown in Fig. 1.

Table 2. Results from hydrogen evolution technique(Calculated values of the rate of hydrogen evolution, inhibition efficiency, activation energy, enthalpy change and entropy change for MS in 5.0 M H_2SO_4 solutions containing *Phyllanthus fraternus* leaves extract)

Concentration of inhibitor (g/l)	Rate of hydrogen evolution cm^3/min.			Inhibition efficiency (%)			Ea kJ/mol	ΔH^0 kJ/mol	ΔS J mol^{-1}K^{-1}
	30^{o}C	40^{o}C	50^{o}C	30^{o}C	40^{o}C	50^{o}C			
0	0.6	1.71	2.68	-	-	-	57.69	-55.49	-61.35
0.5	0.45	1.49	2.41	25	12.86	10.07	59.28	-56.98	-57.12
1.0	0.32	1.25	2.10	46.67	26.9	21.65	61.54	-58.78	-53.19
2.0	0.24	0.96	1.85	60	43.85	30.97	64.65	-61.32	-41.89
3.0	0.19	0.65	1.32	68.33	61.98	50.75	66.29	-64.66	-38.76
4.0	0.12	0.42	0.92	80	75.43	65.67	69.18	-66.21	-35.12

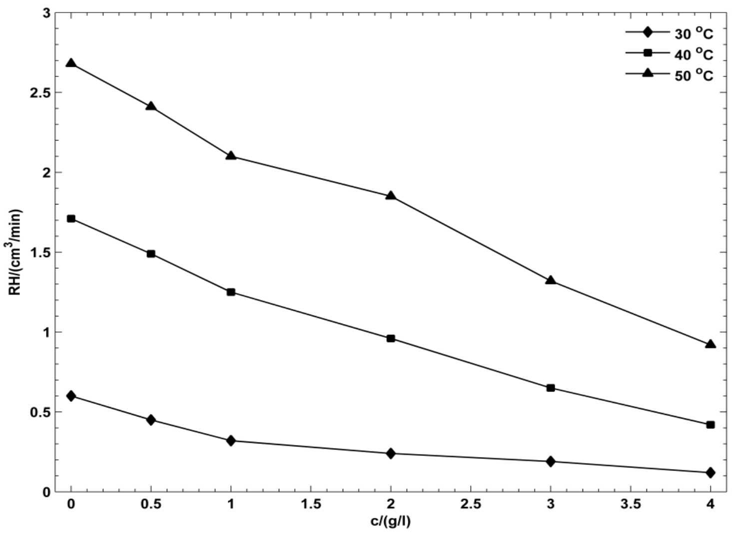

Figure 1. Rate of hydrogen evolved for the various extract concentration in 5.0 M H_2SO_4 solutions using hydrogen evolution technique

The results attained (Table 2) show that the inhibition efficiencies increase with increase in *Phyllanthus fraternus* leaves extract concentration and decrease slightly with increase in temperature.

3.3. Activation parameters

The activation parameters for MS in 5.0 M H_2SO_4 solutions in the absence and presence of *Phyllanthus fraternus* leaves extract were calculated from the Arrhenius-type plot (Eq. (5)) and the transition state Eq. (6)

$$k = A\exp\left(-E_a/RT\right) \tag{5}$$

$$k = RT/Nh\exp\left(\Delta S^0/R\right)\exp\left(-\Delta H^0/RT\right) \tag{6}$$

where R is the universal gas constant, N is the Avogadro's number, h is the Plank's constant, E_a is the activation energy, T is the absolute temperature, and ΔH^o and ΔS^o are the standard enthalpy and entropy of activation, respectively.

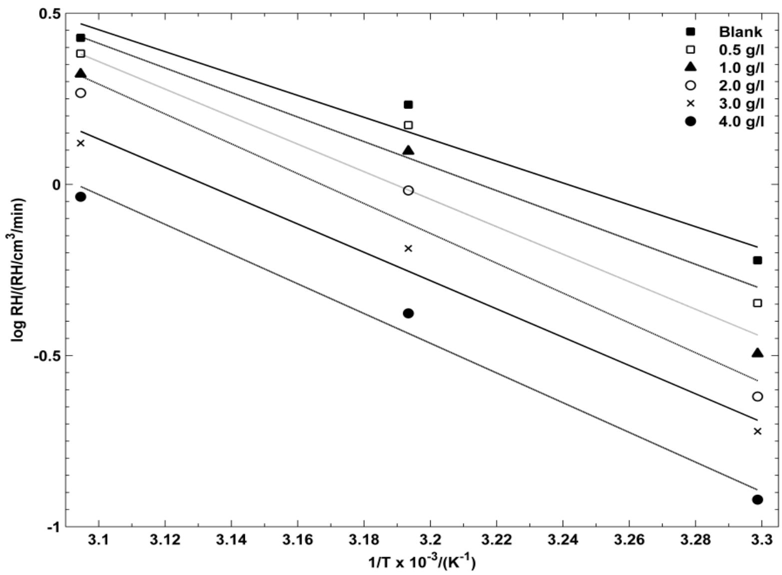

Figure 2. Arrhenius plot for MS in 5.0 M H_2SO_4 solutions containing *Phyllanthus fraternus* leaves extract

From Fig. 2, the activation energies is obtained from the slopes of the plots and listed in Table 2. From the results, it is observed that E_a values increased in presence of the plant extract in relation to the blank system. The maximum Ea value at highest concentration of plant extract is 69.18 kJ/mol which confirmed the physical adsorption mechanism. The enthalpy and the entropy of activation values for MS in 5.0 M H_2SO_4 solutions obtained from linear square fit of log (*RH/T*) data versus 1/*T* (Fig. 3) are presented in Table 2. The negative values of ΔH^o obtained represent an exothermic adsorption process. This suggests either physical or chemical adsorption. Usually, the enthalpy of physical adsorption process is lower than 80 kJ/mol while the enthalpy of chemisorption process approaches 100 kJ/mol. Hence, the ΔH^o *values obtained confirm the* physical adsorption of the plant extract constituents on the surface of MS. The negative ΔS^o values suggest that, the activation complex in the rate determining step represents association rather than dissociation step [21-22].

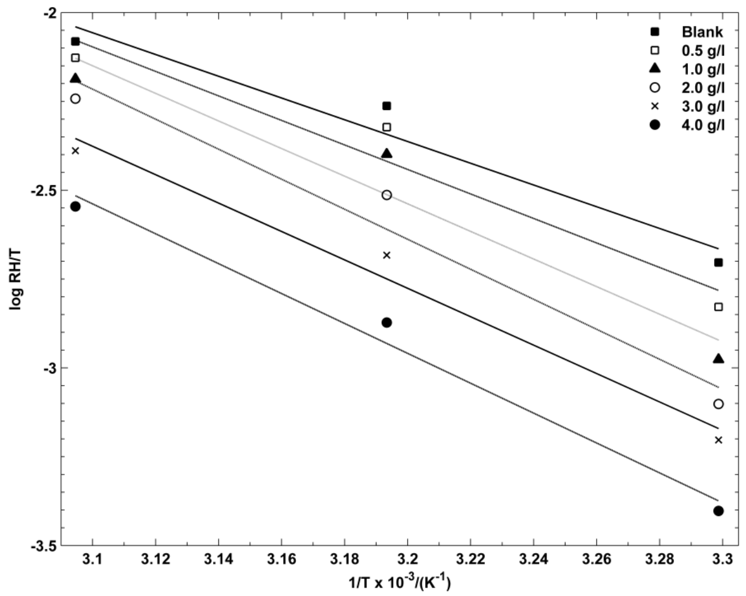

Figure 3. Transition state plot for MS in 5.0 M H_2SO_4 solutions containing *Phyllanthus fraternus* leaves extract

3.4. Electrochemical polarizations

The potentiodynamic polarization data are shown in Fig. 4as the Tafel plots for MS in 1 M H_2SO_4 solutions with the addition of various concentrations of the additive. The corrosion kinetic parameters such as E_{corr}, I_{corr}, anodic and cathodic Tafel slopes (b_a and b_c) were derived from these curves and are given in Table-3. The values of E_I % were calculated using the following equation.

$$E_I\% = 100 \times \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \quad (7)$$

Where I_{corr} and $I_{corr(inh)}$ are the values of corrosion current densities of MS without and with the additive, respectively.

The inhibiting properties of *Phyllanthus fraternus* leaves extract have also been evaluated by determining the values of R_p. The corresponding R_p values of MS in 1 M H_2SO_4 solutions, in the absence and presence of different concentrations of the extract, are given in Table-3. The values of IE (E_{Rp}%) were calculated as follows:

$$E_{Rp}\% = 100 \times \frac{R_{P(inh)} - R_P}{R_{P(inh)}} \quad (8)$$

R_p and $R_{p(inh)}$ are the polarization resistances in the absence and presence of the additive, respectively.

From the Table-3, it could be found that the I_{corr} values were progressively decreased with steady increase in the concentration of additive up to 4.0g/l from 5.91 to 0.451 mA/cm^2 leading to 92% of IE.

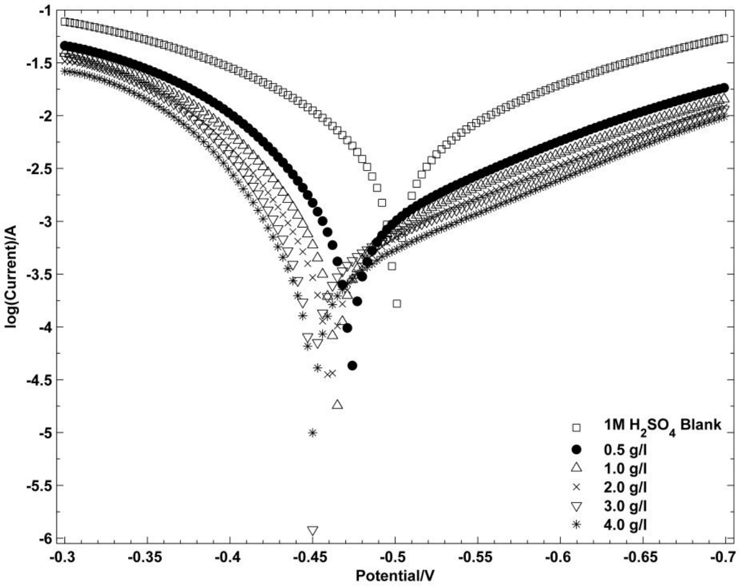

Figure 4. Tafel plots showing effect of increasing concentrations of*Phyllanthusfraternus* leaves extracts on corrosion of MS in H_2SO_4 solutions

Table 3. Effect of *Phyllanthus fraternus*leaves extracts on corrosion of MS in 1 M H_2SO_4 solution studied by electrochemical polarizations in TI and LPR methods

Concentration of inhibitor (g/l)	E_{corr} V	Tafel Constant (mV/decade) ba	bc	I_{corr} (mA/cm^2)	R_p (ohm cm^2)	E_I %	E_{Rp}%
0	-0.4997	143	160	5.914	06	-	-
0.5	-0. 4735	109	150	1.262	21	79	71
1.0	-0.4643	103	150	0.890	29	85	79
2.0	-0.4608	94	148	0.621	39	89	85
3.0	-0.4516	92	149	0.605	43	90	86
4.0	-0.4504	92	148	0.451	57	92	89

The comparison of polarization curves indicated that both cathodic and anodic current were decreased in the presence of *Phyllanthus fraternus* leaves extracts. This inhibitory action suggested that the natural extract may be classified as a mixed type inhibitor. Furthermore, the increase of extract displaced the E_{corr} values towards anodic shift: -0.5V (blank) to -0.45V at 4.0g/l with gradual and significant decrease of anodic Tafel slope, b_a =143 mV/decade of blank to 92 mV/ decade. These findings supported the mixed inhibitor with predominance in anodic branche. Cao in his work (1996) resumed the effect of variation of corrosion potential. When the shift of corrosion potential due to addition of an interface inhibitor is negligible, the inhibition is most probably caused by a geometric blocking effect of the adsorbed inhibitive species on the surface of the corroding metal. If ΔE_{corr} is noticeable as in our work, the inhibition effect occurs by blocking the active sites on the metal surface by adsorbed inhibitive species [23]. This effect is due to the changes in the average activation energy barriers of the anodic and cathodic reactions of the corrosion process [23].

The R_p values of MS in 1 M H_2SO_4 solutions in the absence and presence of different concentrations of *Phyllanthus fraternus* leaves extract are also given in Table-3. From the results, it could be seen that the $R_p$values were gradually increased with increase in the concentration of the additive. The difference observed between Efficiency obtained by I_{corr} and R_p is interpreted by the non-applicability of equation (8) when E_{corr} is modified in the presence of inhibitor [23].

3.5. Electrochemical impedance spectroscopy

The corrosion measures of MS in 1 M H_2SO_4solutions, in absence and the presence of various concentrations of *Phyllanthus fraternus* extract were also investigated by EIS technique. The resultant Nyquist plots are shown in Fig 5.There was a gradual increase in the diameter of each semicircle of the Nyquist plots and this increase of the diameters has clearly shown that the R_t values were also increased from 7 to 289 Ohms.cm^2 at the highest concentration of 4.0 g/l due to the formation and gradual improvement in compactness of the barrier layer of the inhibitive molecules (IE 98 %) adsorbed, and as a result the acid corrosion rates of MS were steadily decreased.

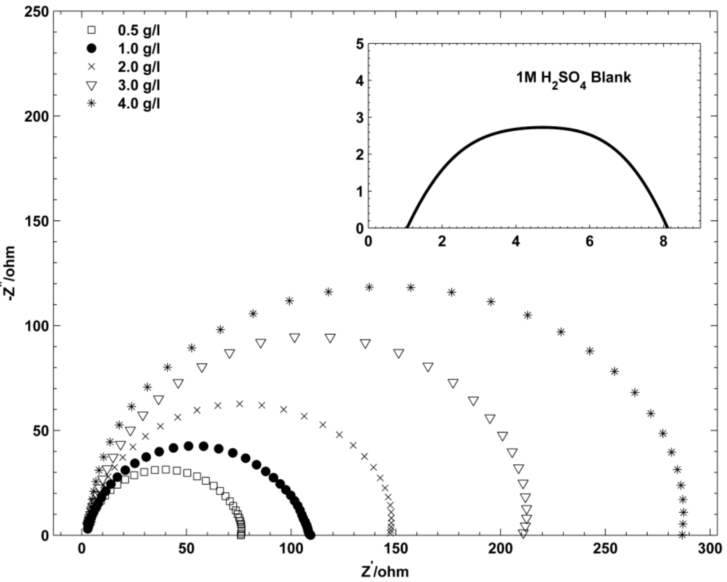

Figure 5. Nyquist plots showing effect of increasing concentration of *Phyllanthus fraternus*leaves extract on corrosion of MS in H_2SO_4 solutions

Table-4 embodies various parameters such as R_t, double layer capacitance (C_{dl}) and IE (E_R %). It was observed that there was a gradual decrease in values of C_{dl} from 155 to 59 μF/cm^2 with increase in the concentration from 0.5 to 4.0 g/l of the extract. The values of E_R % were calculated by the equation as follows:

$$E_R\% = 100 \times \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \quad (9)$$

Where R_t and $R_{t(inh)}$ are charge-transfer resistance values in the absence and presence of the inhibitor, respectively.

To calculate the values C_{dl}, the frequency (f_{max}) at which the imaginary component of the impedance is maximum $-Z_{im(max)}$was found and C_{dl} values were obtained from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_t} \quad (10)$$

Table 4. Data from electrochemical impedance measurements for corrosion of MS in 1 M H_2SO_4 solutions at various concentrations of *Phyllanthus fraternus* leaves extract

Concentration of inhibitor (g/l)	R_t Ohm.cm^2	C_{dl} µF/cm^2	Inhibition Efficiency, E_R %
0	07	155.27	-
0.5	76	89.23	91
1.0	108	83.26	94
2.0	148	73.45	95
3.0	215	66.21	97
4.0	289	59.18	98

The stability of the barrier layer formed by the adsorbed molecules of *Phyllanthus fraternus* leaves extract was very good when there were no DC polarizations exerted in AC Impedance method but in the WL and gasometric measurements when the highest temperature of 50^{o}C and the DC polarizations at ambient temperature were carried out, the stability of the layers was considerably decreased due to removal of the loosely adsorbed molecules on the steel surface. The good inhibitory of natural extract may be due to the synergistic intermolecular effect of the various components screened and presented in Table 5 [24-26].

Table 5. Phytochemical constitute of *Phyllanthus fraternus* leaves extract

Chemical constitute	Screening
Alkaloid	Present
Tannins	Present
Saponins	Present
Phlobatannins	Absent
Terpenoid	Present
Glycosides	Absent
Steroid	Present

4. CONCLUSIONS

- The active molecules present in the extract of *Phyllanthus fraternus*leaves have effectively inhibited corrosion of MS in 1 M H_2SO_4 by forming a protective barrier layer. The inhibition efficiency of the extract increased gradually with increase in its concentration.

- Polarization measurements have shown that the extract of *Phyllanthus fraternus* leaves has acted as a mixed type corrosion inhibitor, retarding mainly anodic dissolution of steel in 1 M H_2SO_4.
- The results of the weight loss, gasometric measurements, electrochemical polarization and AC impedance spectroscopy were all in very good agreement to support the above conclusions.

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