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Research Article

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Corrosion Inhibition of Mild Steel by *Stachytarpheta Indica* Leaf Extract in Acid Medium

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Abstract *Stachytarpheta indica* leaf extract inhibited the corrosion of mild steel in 1M H_2SO_4 solution by both gravimetric and hydrogen evolution methods. The inhibition efficiency increased with increase in the leaf extract concentration and decrease in temperature. Physical adsorption has been proposed for the adsorption of *Stachytarpheta indica* leaf extract on mild steel surface. The adsorption of the leaf extract obeyed the modified Langmuir adsorption isotherm. The calculated thermodynamic parameters revealed that the corrosion inhibition process was both endothermic and spontaneous.

Keywords Physical adsorption, Langmuir isotherm, Gravimetric, Hydrogen evolution

Introduction

The corrosion of metals, though a natural phenomenon, is undesirable because it weakens the mechanical strength of metals leading to equipment breakdown or failure. In the petroleum industry, oil spillage due to corrosion of pipelines is a common occurrence globally. Of the many methods of combating metallic corrosion, the most cost - effective is the use of corrosion inhibitors [1]. Organic compounds containing N, S and/or S atoms have been reported as potential corrosion inhibitors [2-5]. The problems associated with the traditional inhibitors, which limit their usage nowadays, include biotoxicity, environmentally unfriendly properties, high cost and non-availability on demand. The need for the discovery and/or development of efficient eco-friendly corrosion inhibitors has led to the use of natural substances, especially of plant origin, as corrosion inhibitors. Plant extracts are cheap, biodegradable, renewable and non-toxic. Several leaf extracts have been reported as good inhibitors of mild steel corrosion in acidic media [6-9]. The search for efficient inhibitors continues because no inhibitor that offers complete protection to mild steel corrosion in either acidic or alkaline medium has been reported.

Stachytarpheta indica belongs to the family Verbenaceae. It's English name is Aeron's rod or Brazilian tea. Among the Efik/Ibibio speaking people of Nigeria, it is called Aran Umon. It is a highly valuable plant used traditional by the people of south eastern Nigeria for the treatment of malaria. Previous work [10] revealed the presence of phlobotanin, saponin, tannins, proteins, carbohydrates and alkaloids in *Stachytarpheta indica* leaf extract. The presence of these phytochemicals (containing organic N, S and O atoms in the combined form) indicate the likelihood of *Stachytarpheta indica* leaf extract being a potential corrosion inhibitor. This work aims at inhibiting the corrosion of mild steel in 1M H_2SO_4 solution using *Stachytarpheta indica* leaf extract.

Materials and Methods

Test materials

Mild steel sheet used for this work was obtained in Calabar, Nigeria. The sheet was mechanically press cut into 5 cm x 4 cm x 0.5 cm coupons. These coupons were polished to mirror finish using different grades of silicon carbide papers. The coupons were degreased in absolute ethanol, dried in acetone and stored in a moisture–free desiccator before use in corrosion studies.

Preparation of *Stachytarpheta indica* leaf extract

Fresh leaves of *Stachytarpheta indica* were collected from a farm in Etinan Local Government Area of Akwa Ibom State, Nigeria. They were plucked, washed and shade – dried at 30 °C for seven days. They were then ground to powder. The dried ground samples of *Stachytarpheta indica* leaves were macerated with 90% ethanol for seven days at room temperature in a large glass trough with cover. The mixture was then filtered. The filtrate was evaporated at 40°C in a water bath to constant weight, leaving a dark green extract in the beaker. Extract concentrations of 1.0 g/L, 2.0 g/L, 3.0 g/L, and 4.0 g/L respectively in 1M H_2SO_4 solution were used for the gravimetric method at 30 -60 °C. The same extract concentrations were used in 1M H_2SO_4 solution for the hydrogen evolution tests.

Gravimetric method

The apparatus and procedure followed for the gravimetric method were as previously reported [11]. The corrodent concentration was 1.0M H_2SO_4 and the volume of the test solution used was 100 mL. All tests were made in aerated solutions. The difference between the weight at a given time and the initial weight of the coupons was taken as the weight loss which was used to compute the corrosion rate given by [12]:

$$CR\ (mg\ cm^{-2} hr^{-1}) = \left(\frac{W}{A\ t}\right) \qquad (1)$$

where *W* is the weight loss (mg), A is the surface area of the specimen (cm^2) while *t* is the exposure time (hr).

The inhibition efficiency (I%) of *Stachytarpheta indica* leaf extract acting as inhibitor in 1.0 M H_2SO_4 was calculated using the formula:

$$\%I = 100\ X \left(\frac{W_0 - W_1}{W_0}\right) \qquad (2)$$

where W_0 and W_1 are the weight losses of the mild steel coupons in the absence and presence of inhibitors, respectively, in 1.0M H_2SO_4 solution at the same temperature.

Hydrogen evolution method

The reaction vessel and procedure for measuring the corrosion process by this method has been described by other authors [13]. A 100 cm^3 of 1M H_2SO_4 solution was introduced into the reaction vessel connected to a burette through a delivery tube. The initial volume of air in the burette was recorded. Two mild steel coupons weighing 8.0g were dropped into the 1M H_2SO_4 solution and the reaction vessel quickly closed to prevent any escape of hydrogen gas.

The volume of H_2 gas evolved from the corrosion reaction was monitored by the depression (in cm3) in the paraffin oil level. The depression in paraffin oil level was monitored every 60 seconds for 100 minutes. The same experiment was repeated in the presence of 1.0 g/L – 4.0 g/L *Stachytarpheta indica* leaf extract (inhibitor) in 1M H_2SO_4 solution.

The inhibition efficiency (%I) was calculated using the equation [14]:

$$I(\%) = \left(\frac{V_0 - V_1}{V_0}\right) \times 100 \qquad (3)$$

where V_0 and V_1 are the volumes of H_2 gas evolved in the absence and presence of inhibitor, respectively, at a specified time.

Results and Discussion

Effect of extract concentration on inhibition efficiency

Figure 1 shows that *Stachytarpheta indica* leaf extract appreciably inhibited the corrosion of mild steel in 1.0M H_2SO_4 solution by weight loss measurements. It is observed that, at a particular temperature, the inhibition efficiency increased with increase in extract concentration. An increase in inhibition efficiency with increase in extract (inhibitor) concentration indicates a strong interaction between the extract and metal surface.

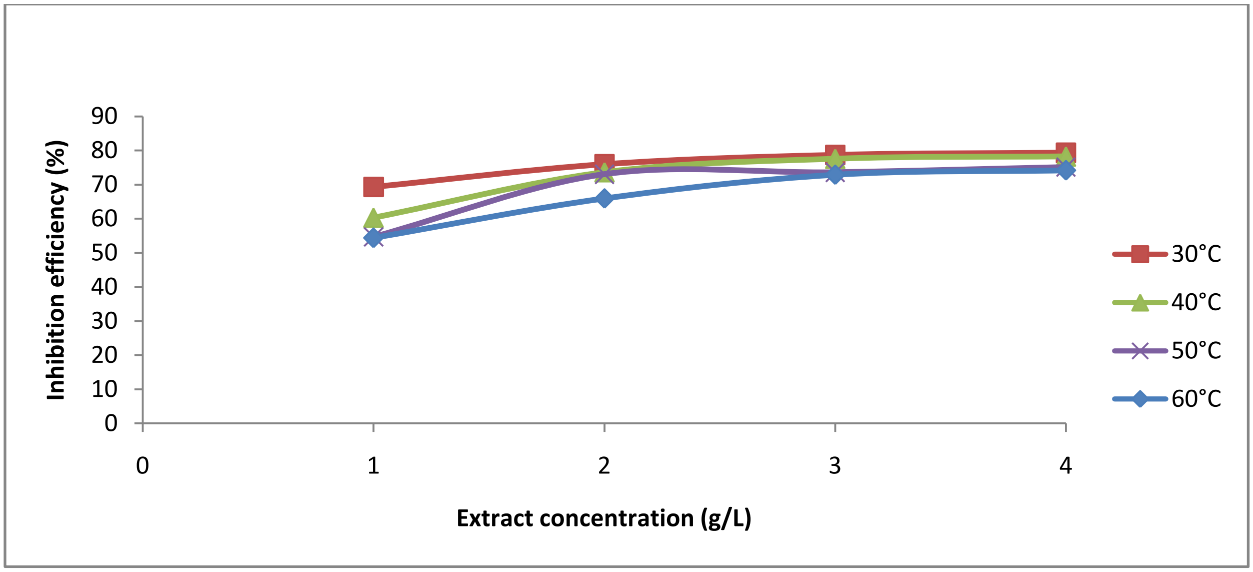

Figure 1: Effect of Stachytarpheta indica leaf extract concentration on the inhibition efficiency of mild steel corrosion in 1M H_2SO_4 at different temperatures

Hydrogen evolution measurements

Figure 2 illustrates the effect of *Stachytarpheta indica* leaf extract on the volume of H_2 gas evolved in the corrosion of mild steel in 1M H_2SO_4. It is observed that as the leaf extract concentration increases, the volume of H_2 gas evolved decreases, at a given time. Table 1 contains the calculated values of inhibition efficiency for the inhibition process containing *Stachytarpheta indica* leaf extract. Table 1 reveals that the inhibition efficiency increased with increase in the concentration of *Stachytarpheta indica* leaf extract. A similar trend was observed in the weight loss method.

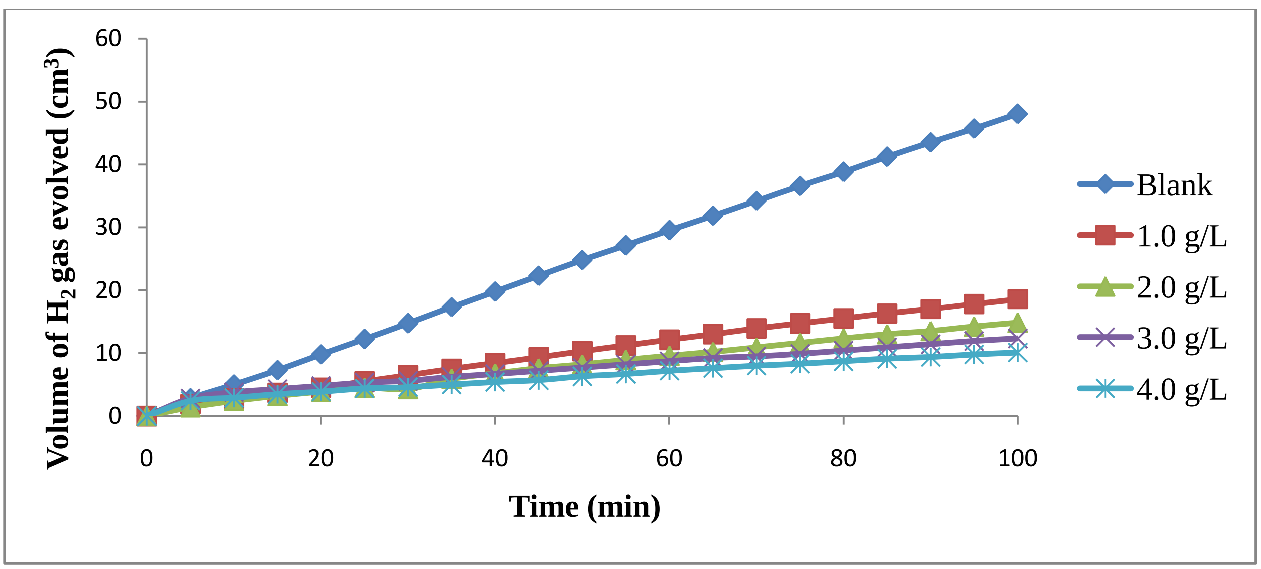

Figure 2: Variation of volume of H_2 gas evolved (cm^3) with time (min) for mild steel corrosion in 1M H_2SO_4 in the absence and presence of Stachytarpheta indica leaf extract at 30°C

Table 1: Effect of *Stachytarpheta indica* leaf extract concentration on inhibition efficiency of mild steel in 1M H_2SO_4 solution at 30°C (Hydrogen evolution measurements)

Extract concentration	Volume of H_2 evolved (cm^3)	Time taken (min)	Inhibition efficiency (%)
1M H_2SO_4 (Blank)	48.0	100	-
1.0 g/L	18.6	100	61.25
2.0 g/L	14.8	100	69.17
3.0 g/L	12.3	100	74.38
4.0 g/L	10.1	100	78.96

Effect of temperature on inhibition efficiency

The inhibition efficiency of *Stachytarpheta indica* leaf extract decreased with increase in temperature (Table 2). This indicates a weakening of adsorption bonds between metal surface and inhibitor as well as a physical adsorption mechanism [11].

Table 2: Calculated values of corrosion rate and inhibition efficiency for mild steel corrosion in 1M H_2SO_4 in the absence and presence of different concentrations of *Stachytarpheta indica* leaf extract

Extract conc	Weight loss (g)				Corrosion rate (mg cm^{-2} hr^{-1})				Inhibition efficiency (%)			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
Blank	0.329	0.630	0.898	2.068	2.0563	3.9375	5.6125	12.9250	-	-	-	-
1.0 g/L	0.101	0.250	0.407	0.944	0.6313	1.5625	2.5438	5.9000	69.30	60.32	54.68	54.35
2.0 g/L	0.079	0.164	0.242	0.704	0.4938	1.0375	1.5125	4.4017	75.99	73.65	73.05	65.96
3.0 g/L	0.070	0.137	0.237	0.560	0.4375	0.8813	1.4813	3.5000	78.72	77.62	73.61	72.92
4.0 g/L	0.068	0.137	0.223	0.534	0.4250	0.8563	1.3938	3.3375	79.33	78.25	75.17	74.18

The thermodynamic parameters for mild steel corrosion in 1M H_2SO_4 in the absence and presence of different concentrations of *Stachytarpheta indica* leaf extract were obtained by using the Arrhenius equation [eq. (4)] and transition state equation [eq.(5)], respectively.

$$CR = Ae^{-E_a/RT} \tag{4}$$

$$CR = (RT/Nh)\, exp(\Delta S^0/R)\, exp(-\Delta H^0/RT) \tag{5}$$

where CR is the corrosion rate, E_a is the activation energy, ΔH^0 is the enthalpy of adsorption, ΔS^0 is the entropy of adsorption, N is the Avogadro's number and h is the Planck's constant.

The E_a values presented in Table 3 were obtained from the gradients ($-E_a/R$) of the linear plot of ln CR vs. 1/T (Arrhenius plot) for mild steel corrosion in 1M H_2SO_4 in the absence and presence of *Stachytarpheta indica* leaf extract (Figure 3**)**.

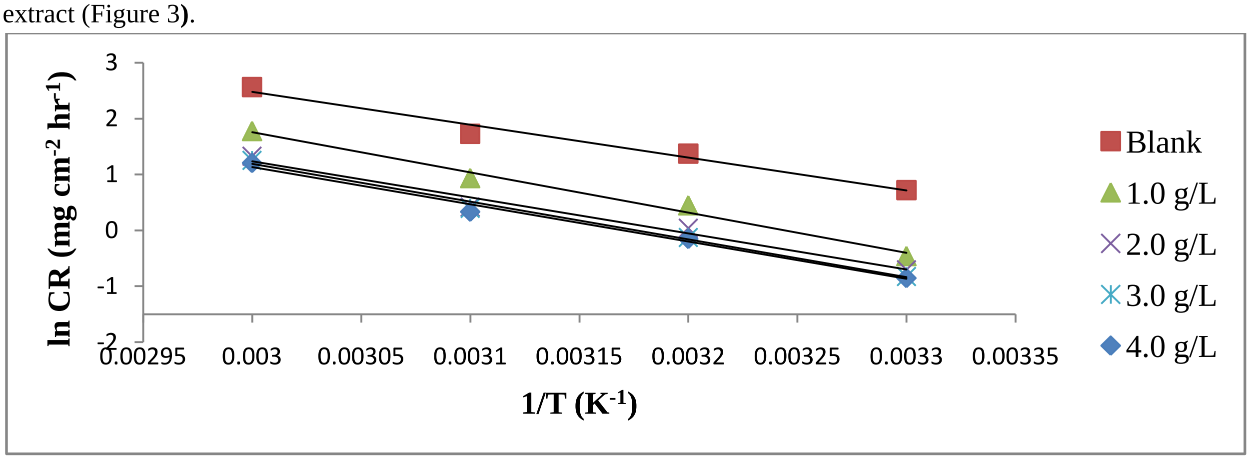

Figure 3: Plot of ln CR vs. 1/T (Arrhenius plot) for mild steel corrosion in 1M H_2SO_4 in the absence and presence of Stachytarpheta indica leaf extract

Table 3: Thermodynamic parameters for mild steel corrosion in 1M H_2SO_4 in the absence and presence of *Stachytarpheta indica* leaf extract

Extract concentration	E_a (kJ mol^{-1})	ΔH^0_{ads} (kJ mol^{-1})	ΔS^0_{ads} (J K^{-1} mol^{-1})
1M H_2SO_4 (Blank)	48.7982	46.1793	-86.7217
1.0 g/L	59.7976	57.1787	-59.7261
2.0 g/L	57.6975	55.0811	-69.3870
3.0 g/L	56.1843	53.5663	-75.2650
4.0 g/L	55.4527	52.8371	-77.9088

The ΔH^0_{ads} and ΔS^0_{ads} values also presented in Table 3 were obtained from the gradients ($-\Delta H^0/R$) and intercepts {ln (R/Nh) + $\Delta S^0/R$}, respectively, of the linear plot of ln (CR/T) vs. 1/T (transition state plot) (Figure 4). From Table 3, the E_a values in the presence of the extract were higher than in the blank. An increase in the E_a values in the presence of the extract (inhibitor) compared to the blank indicates the ability of the extract to increase the energy barrier of the electrochemical reactions and thus slows down the corrosion process. The ΔH^0_{ads} values presented in Table 3 are positive while the ΔS^0 values are negative. The positive values of ΔH^0_{ads} reveal that the adsorption of the extract on mild steel surface was endothermic in nature. Conversely, the negative values of ΔS^0_{ads} indicate a decrease in the disorderliness of the system.

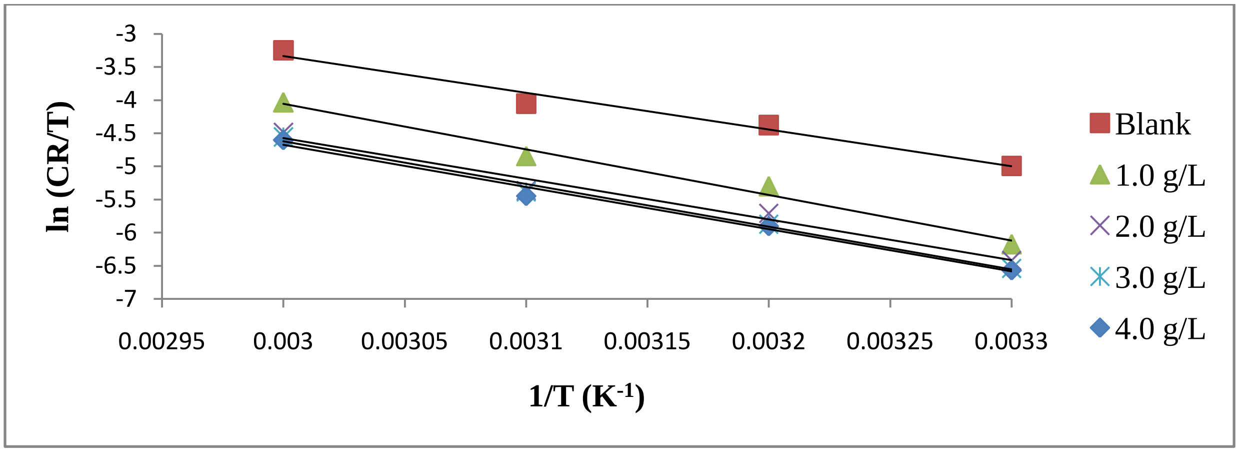

Figure 4: Plot of ln (CR/T) vs. 1/T (Transition state plot) for mild steel corrosion in 1M H_2SO_4 solution in the absence and presence of Stachytarpheta indica leaf extract

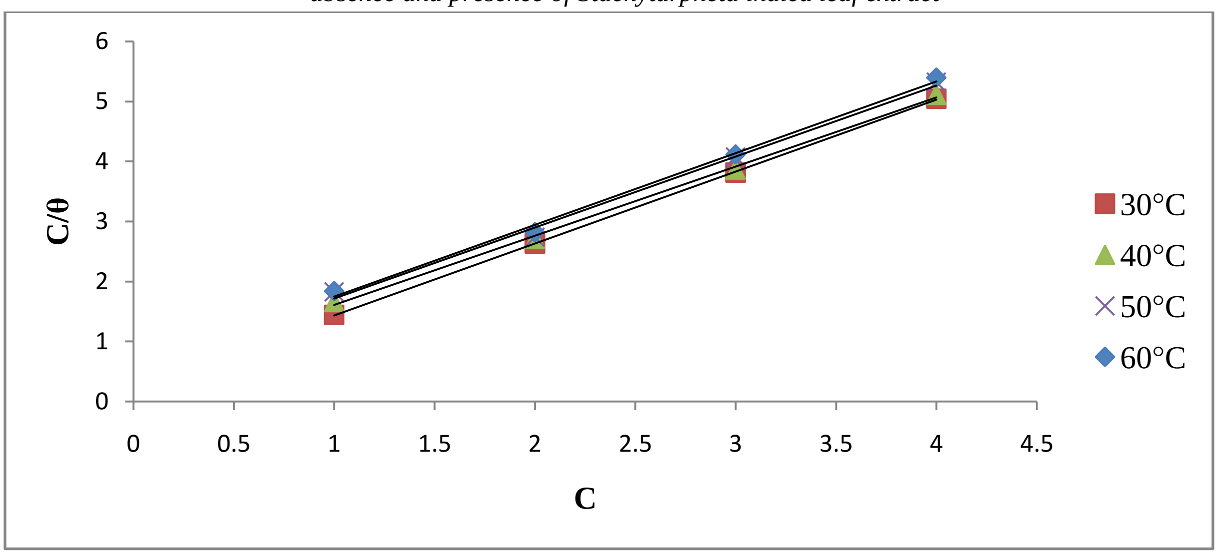

Figure 5: Plot of C/θ vs. C (Langmuir isotherm) for mild steel corrosion in 1M H_2SO_4 solution containing Stachytarpheta indica leaf extract

Adsorption studies

The best fit for the adsorption of *Stachytarpheta indica* leaf extract on mild steel surface occurred via the modified Langmuir adsorption isotherm defined as [15]:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \quad (6)$$

where C is the inhibitor concentration, θ is the degree of surface coverage while K_{ads} is the equilibrium constant of the adsorption process. Plot of C/θ vs. C gave straight lines (Figure 5).

The values of K_{ads} were evaluated from the intercept of the graph and presented in Table 4. K_{ads} is related to the standard free energy of adsorption (ΔG^0_{ads}) by the formula:

$$\Delta G^0_{ads} = -RT\ ln(55.5 K_{ads}) \quad (7)$$

where 55.5 is the molar concentration of water in the solution in mol dm^{-3}.

The negative values of ΔG^0_{ads} for the leaf extract indicate the spontaneity of the adsorption process. Additionally, values of ΔG^0_{ads} less negative than -20 $kJmol^{-1}$ are attributed to electrostatic interaction between the charged inhibitor and the charged metal surface implying a physical adsorption process. Conversely, values of ΔG^0_{ads} less negative than -40kJ mol^{-1} are generally considered to involve charge sharing between the inhibitor and the metal surface and signifies a chemical adsorption process [16]. The values of ΔG^0_{ads} in this work being less negative than -20kJ mol^{-1} coupled with a decrease in the inhibition efficiency with increase in temperature indicates that the adsorption of *Stachytarpheta indica* leaf extract on mild steel surface occurred by a physical adsorption mechanism.

Table 4: Parameters of the linear regression of Langmuir adsorption isotherm

Temperature	R^2	n	$1/K_{ads}$	K_{ads}	ΔG^0_{ads} (kJ mol^{-1})
30°C	0.9999	1.20	0.2379	4.2034	-13.7351
40°C	0.9987	1.15	0.4597	2.1753	-12.4742
50°C	0.9940	1.18	0.5371	1.8619	-12.4549
60°C	0.9991	1.17	0.6598	1.5156	-12.2708

Conclusion

Stachytarpheta indica leaf extract acted as an inhibitor for mild steel corrosion in 1M H_2SO_4 solution. The inhibition efficiency increased with increase in extract concentration but decreased with increase in temperature. The *Stachytarpheta indica* leaf extract adsorbed on mild steel surface following the Langmuir adsorption isotherm. The values of ΔG^0_{ads} were negative which indicated the spontaneity of the adsorption process. Physical adsorption mechanism has been proposed for the adsorption of *Stachytarpheta indica* leaf extract on mild steel surface. Thermodynamic parameters revealed that the adsorption process was both endothermic and spontaneous.

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