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Research Article

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Jatropha tanjorensis Leaf Extract as an Environmentally – Friendly Mild Steel Corrosion Inhibitor in H_2SO_4 Solution

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Abstract The inhibition of the corrosion of mild steel in 1 M H_2SO_4 solution by *Jatropha tanjorensis* leaf extract (JTLE) has been studied using weight loss and hydrogen evolution techniques. The results obtained reveal that JTLE effectively inhibited the corrosion of mild steel in H_2SO_4 solution. The highest inhibition efficiency of 89.73% occurred at 5.0 g/L JTLE concentration at 333K by weight loss measurements. Inhibition efficiency was found to increase with increase in JTLE concentration and temperature. Chemical adsorption has been proposed for the adsorption of JTLE onto mild steel surface. The positive values of enthalpy of adsorption ($\Delta H°_{ads}$) reveal the endothermic nature while the negative values of Gibb's free energy of adsorption ($\Delta G°_{ads}$) indicate the spontaneous nature of adsorption of JTLE onto mild steel surface. The adsorption of JTLE onto mild steel surface obeyed the Langmuir adsorption isotherm.

Keywords *Jatropha tanjorensis*, Mild steel, Extract, Langmuir isotherm, Chemisorption

1. Introduction

Pickling is one of the industrial processes where a metal is dipped into a concentrated mineral acid solution. The pickling of mild steel in acid medium inadvertently leads to its corrosion in the pickle liquor. The desire by scientists to reduce the corrosion of metals in such an aggressive environment using environmentally - friendly metal corrosion inhibitors is yielding positive results, with the extraction of promising corrosion inhibitors from natural products [1]. Some of the reported environmentally- friendly inhibitors of mild steel corrosion in acidic medium include rice husk extract [2], dyes [3], polymers [4 - 5], coffee extract [6], exudate gum [7], leaf extracts [8 - 9], amongst others. This work is our contribution to the global search for efficient environmentally - friendly inhibitors of mild steel corrosion in acidic medium. *Jatropha tanjorensis* plant belongs to the family Euphorbiaceae. Its leaves are eaten as a vegetable and also used in traditional medicine by the people of southern Nigeria. The phytochemical analysis of *Jatropha tanjorensis* leaf extract reveal the presence of alkaloid, anthraquinone, tannin, cardiac glycoside, saponin and flavonoid [10].There is no reported work on the inhibition of mild steel corrosion in acidic medium by *Jatropha tanjorensis* leaf extract. The aim of this work was to assess the inhibitory effect of *Jatropha tanjorensis* leaf extract on mild steel corrosion in H_2SO_4 solution.

2. Materials and Methods

2.1. Test Materials

The chemical composition of the mild steel sheet used for this study was as follows (weight %): C (0.12), Mn (0.85), S (0.06), P (0.05), Si (0.09) and Fe (98.83). The sheet was mechanically press - cut into 4 cm x 5 cm coupons, and polished to mirror finish using different grades of silicon carbide papers. The coupons were degreased in absolute ethanol, dipped in acetone before air-drying. They were then stored in a moisture – free desiccator before use in corrosion studies [11].

2.2. Preparation of *Jatropha tanjorensis* leaf extract

Jatropha tanjorensis leaves were collected from a farm in Ikot Ekpene, Akwa Ibom State, Nigeria and authenticated by a plant taxonomist in the Department of Botany and Ecological Studies, University of Uyo, Nigeria. They were washed and air – dried at 30°C for seven days and ground to powder. The *Jatropha tanjorensis* leaf extract was obtained following standard procedure reported previously [8,12].

2.3. Weight loss method

The mild steel coupons were suspended with the aid of glass hooks and rods and immersed in 100 cm^3 of 1 M H_2SO_4 solution (blank) and in 1 M H_2SO_4 solution containing 0.5 g/dm^3 – 5.0 g/dm^3 *Jatropha tanjorensis* leaf extract (inhibitor) in open beakers. One mild steel coupon per beaker was used in each experiment. The beakers were then placed in a thermostatic water bath maintained at 30°C, 40°C, 50°C, and 60°C, respectively. The mild steel coupons were retrieved from the test solutions after four (4) hours and scrubbed with bristle brush under running water. They were dipped in acetone and air - dried before reweighing.

The inhibition efficiency I_{WL} (%) was calculated using the formula:

$$I_{WL}(\%) = \left(1 - \frac{W_1}{W_0}\right) \times 100 \quad (1)$$

where W_0 is the weight loss (g) of the mild steel coupons in the absence of extract while W_1 is the weight loss (g) of the mild steel coupons in the presence of extract in 1 M H_2SO_4 at the same temperature.

The corrosion rate (CR) of mild steel in 1 M H_2SO_4 was calculated via the equation [9]:

$$\text{CR}\ (\text{mg cm}^{-2}\text{hr}^{-1}) = \left(\frac{W}{At}\right) \quad (2)$$

where A is the total surface area (cm^2), W is the weight loss (mg) while t is the exposure time (hours).

2.4. Hydrogen Evolution Method

The hydrogen evolution tests were done using similar equipment and procedure as reported by other workers [13]. The volume of the acid used was 100 cm^3 of 1 M H_2SO_4 solution. One mild steel coupon weighing 4.0 g was dropped into the 1 M H_2SO_4 solution. The volume of H_2 gas evolved (cm^3) in the corrosion process was recorded every 60 seconds for 20 minutes. The experiment was repeated in the presence of 0.5 g/dm^3 – 5.0 g/dm^3 *Jatropha tanjorensis* leaf extract in 1 M H_2SO_4 solution.

The inhibition efficiency I_{HE} (%) was calculated using the equation [1]:

$$I_{HE}(\%) = \left(1 - \frac{R_{H1}}{R_{H0}}\right) \times 100 \quad (3)$$

where R_{H0} is the rate of evolution of H_2 gas in the absence of inhibitor and R_{H1} is the rate of evolution of H_2 gas in the presence of inhibitor, respectively, at a specified time.

3. Results and Discussion

3.1. Effect of *Jatropha tanjorensis* leaf extract concentration on inhibition efficiency

Fig. 1 depicts the effect of *Jatropha tanjorensis* leaf extract (JTLE) concentration on inhibition efficiency of mild steel corrosion in 1 M H_2SO_4 at 30°C - 60°C by the weight loss method. It is observed that, at a given temperature, the inhibition efficiency increased with increase in JTLE concentration. Fig. 2 shows a decrease in the volume of hydrogen gas evolved with increase in JTLE concentration. The higher the concentration of JTLE, the lower the volume of H_2 gas evolved; the lower the volume of H_2 gas evolved, the higher the inhibition efficiency (Table 1). An increase in the inhibition efficiency with increase in JTLE concentration is an indication of the adsorption of the leaf extract onto mild steel surface. It is note worthy that the inhibition efficiencies by both weight loss and hydrogen evolution methods followed a similar trend.

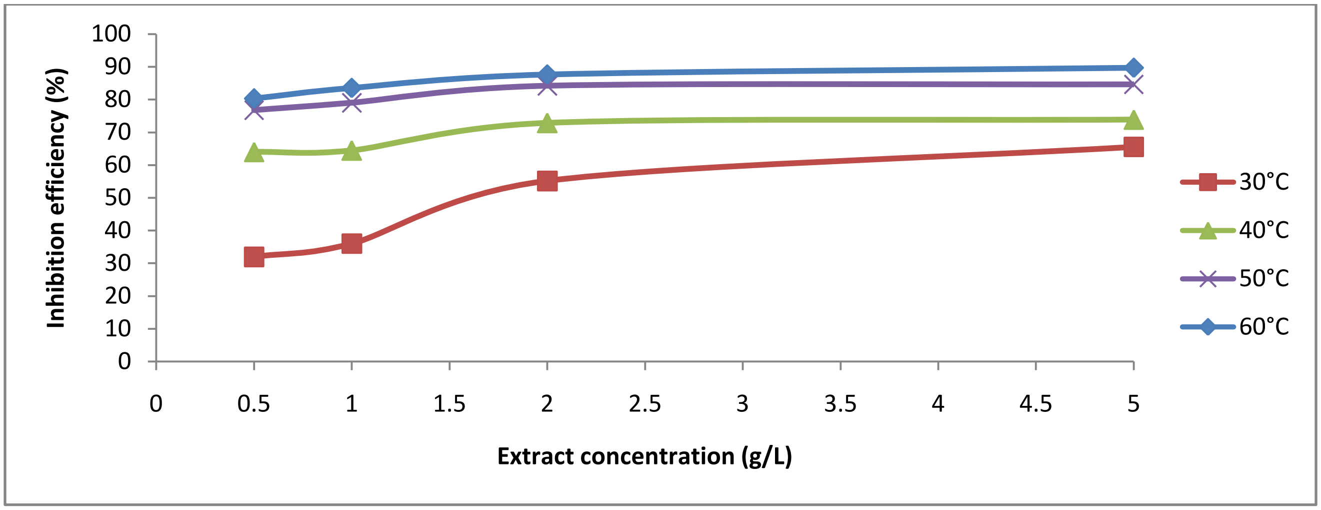

Figure 1: Effect of Jatropha tanjorensis leaf extract (JTLE) concentration on inhibition efficiency for mild steel corrosion in 1 M H_2SO_4 at different temperatures

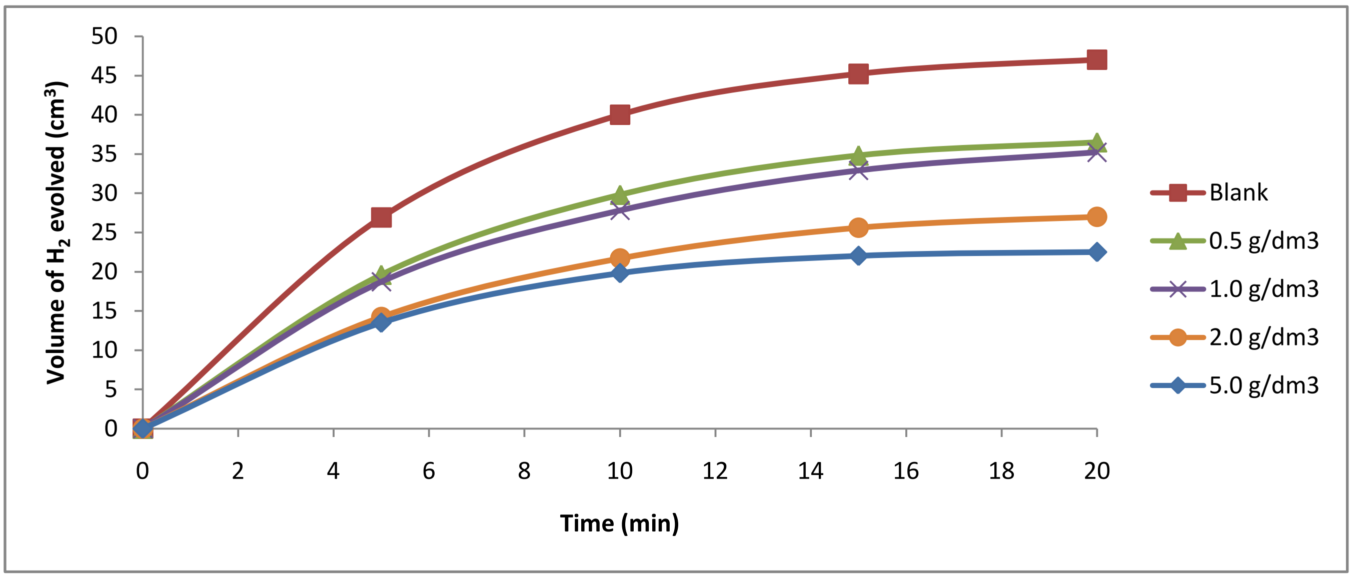

Figure 2: Variation of volume of H_2 gas evolved (cm^3) with time (min) for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of JTLE at 30 °C

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

Extract concentration (g/dm^3)	**H_2 evolution rate (cm^3 min^{-1})**	**Inhibition efficiency (%)**
Blank	2.35	-
0.5	1.83	22.13
1.0	1.76	25.11
2.0	1.35	42.55
5.0	1.13	51.91

3.2. Effect of temperature on inhibition efficiency

Table 2 contains the weight loss data for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of JTLE concentration at 30°C – 60°C. The inibition efficiency was observed to increase with increase in temperature. An increase in inhibition efficiency with increase in temperature indicates that JTLE was more effective as an inhibitor at higher temperatures than at lower temperatures. Furthermore, an increase in inhibition efficiency \with increase in temperature indicates that the inhibitor adsorbed chemically onto mild steel surface.

Table 2: Weight loss data for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of JTLE concentration at 30°C – 60°C

Extract conc. (g/dm^3)	**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	0.2550	0.6897	1.2005	1.9051	1.5937	4.3106	7.5031	11.9069	-	-	-	-
0.5	0.1735	0.2484	0.2791	0.3237	1.0844	1.5525	1.7444	2.0231	31.96	63.98	76.75	83.01
1.0	0.1632	0.2454	0.2522	0.3142	1.0200	1.5337	1.5762	1.9637	36.00	64.42	78.99	83.51
2.0	0.1144	0.1874	0.2309	0.2356	0.7150	1.1712	1.4431	1.4725	55.14	72.83	84.17	87.63
5.0	0.0879	0.1740	0.1780	0.1957	0.5494	1.0875	1.1125	1.2231	65.53	73.84	87.62	89.73

The activation energy (E_a) values for mild steel corrosion in 1 M H_2SO_4 solution in the presence and absence of JTLE, respectively, were calculated using the alternative formulation of Arrhenius equation [14]:

$$\ln CR = \frac{-E_a}{RT} + \ln A \quad (3)$$

where T is the absolute temperature, R is the universal gas constant, CR is the corrosion rate while A is the pre-exponential factor.

The E_a values presented in Table 3 were obtained from the slopes of ln CR against 1/T plots (Figure 3). The E_a values obtained in the presence of *Jatropha tanjorensis* leaf extract were lower than the E_a value of the blank (54.766 kJ mol^{-1}). Lower E_a values in the presence of extract compared to the blank have been attributed to a chemisorption process while the reverse indicates a physisorption process [15]. It could therefore be proposed that the adsorption of JTLE onto mild steel surface occurred by a chemisorption process.

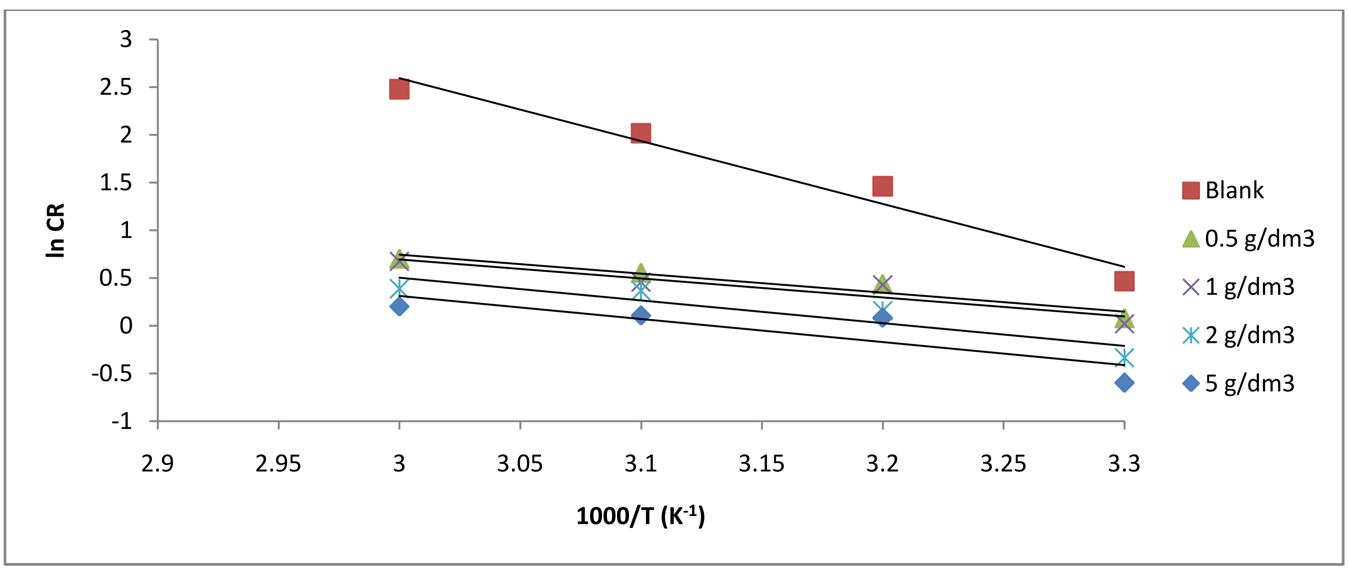

Figure 3: Arrhenius plot for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of Jatropha tanjorensis leaf extract

The values of enthalpy of activation (ΔH°_{ads}) and entropy of activation (ΔS°_{ads}) were obtained using an alternative formulation of the transition state equation [16]:

$$\ln\left(\frac{CR}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^\circ_{ads}}{R}\right] - \frac{\Delta H^\circ_{ads}}{RT} \quad (4)$$

where T is the absolute temperature, CR is the corrosion rate and A is the Arrhenius pre-exponential factor; h is the Planck's constant, R is the universal gas constant and N is the Avogadro's number. Values of ΔH°_{ads} and ΔS°_{ads} were evaluated from the gradients and intercepts of ln (CR/T) against 1/T plots (Figure 4), respectively, and presented in Table 3. An endothermic process is indicated by the positive values of ΔH°_{ads} obtained. Additionally, it could be deduced that a decrease in the disorderliness of the system is indicated by the negative values of ΔS°_{ads} of the system.

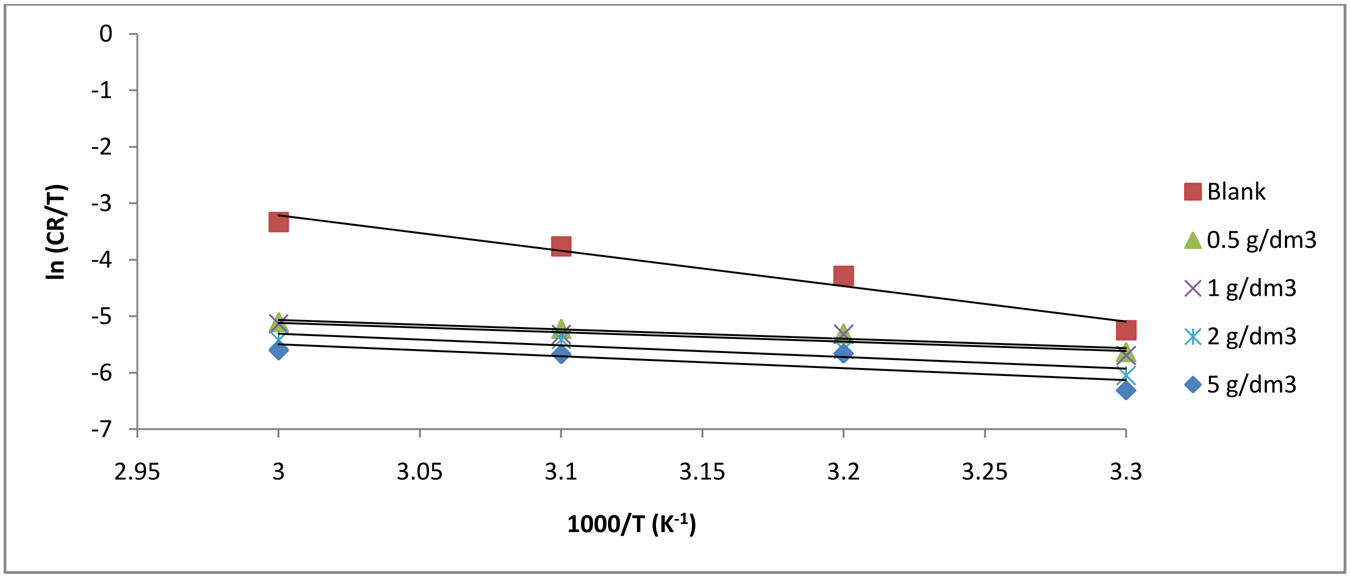

Figure 4: Transition state plot for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of Jatropha tanjorensis leaf extract

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

Extract concentration	E_a (kJ mol^{-1})	ΔH°_{ads} (kJ mol^{-1})	ΔS°_{ads} (J K^{-1} mol^{-1})
1 M H_2SO_4 (Blank)	54.766	52.150	-67.824
0.5 g/dm^3 JTLE	16.525	13.906	-197.932
1.0 g/dm^{3}JTLE	16.566	13.948	-198.223
2.0 g/dm^{3}JTLE	19.756	17.138	-190.258
5.0 g/dm^3 JTLE	20.152	17.538	-190.629

3.3 Adsorption isotherm

The obtained experimental data were tested with several adsorption isotherms. The best fit for the adsorption of *Jatropha tanjorensis* leaf extract onto mild steel surface was found to obey the modified Langmuir adsorption isotherm defined as:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \quad (5)$$

where θ is the degree of surface coverage, C is the inhibitor concentration while K_{ads} is the equilibrium adsorption constant.

The adsorption of *Jatropha tanjorensis* leaf extract on mild steel surface in 1 M H_2SO_4 solution obeyed the Langmuir adsorption isotherm as shown by the linear plot of C/θ against C (Figure 5). The intercepts of the graph were used in determining the values of K_{ads} presented in Table 4. It is observed that the values of K_{ads} increased with increase in temperature. An increase in the values of K_{ads} with increase in temperature is an indication of JTLE becoming more strong adsorbed onto mild steel surface with increase in temperature [16].

The standard free energy of adsorption (ΔG°_{ads}) was calculated using the formula [17,18]:

$$\Delta G^{\circ}_{ads} = -RT\ln(55.5K_{ads}) \quad (6)$$

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

The negative values of ΔG°_{ads} obtained reveal the spontaneity of adsorption of *Jatropha tanjorensis* leaf extract on mild steel surface.

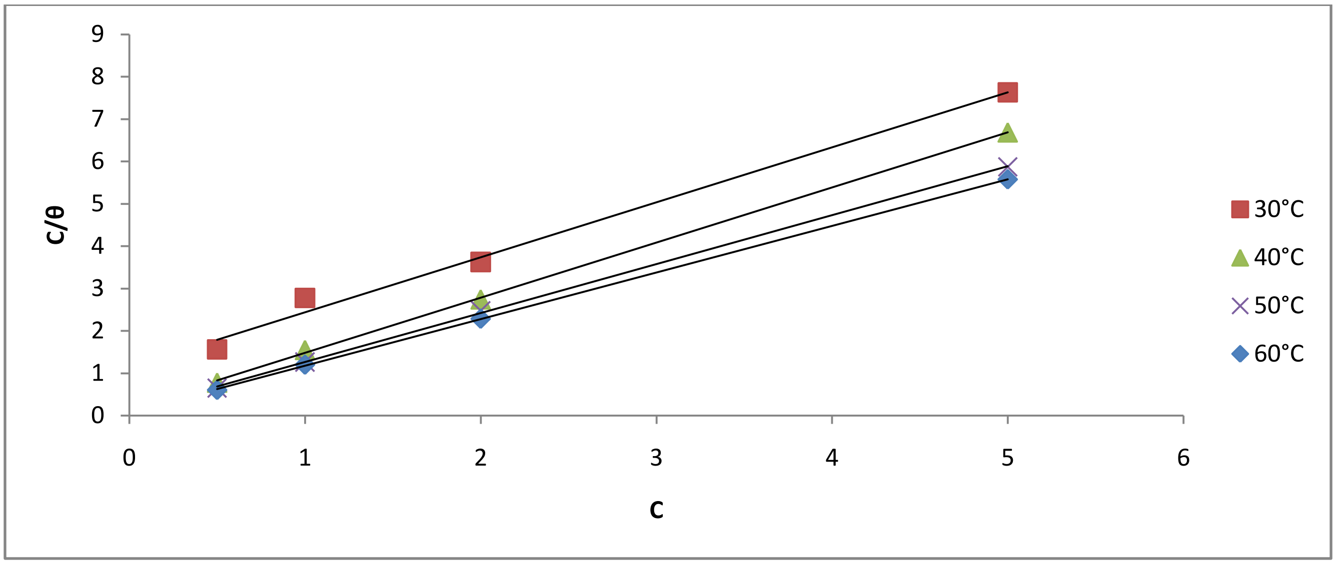

Figure 5: Langmuir isotherm plot for mild steel corrosion in 1 M H_2SO_4 solution containing Jatropha tanjorensis leaf extract

Table 4: Langmuir adsorption parameters for mild steel corrosion in 1 M H_2SO_4 solution containing *Jatropha tanjorensis* leaf extract

Temperature	R^2	n	$1/K_{ads}$ (g dm^{-3})	K_{ads}($g^{-1}dm^3$)	ΔG°_{ads} (kJ mol^{-1})
303K	0.9914	1.30	1.1422	0.8755	-9.783
313K	0.9996	1.30	0.1754	5.7013	-14.982
323K	0.9997	1.16	0.1101	9.0827	-16.711
333K	0.9999	1.10	0.0756	13.2275	-18.269

Conclusion

On the basis of this study, the following conclusions could be drawn:

1. *Jatropha tanjorensis* leaf extract appreciably inhibited the corrosion of mild steel in H_2SO_4 solution.
2. The inhibition efficiency increased with increase in extract concentration and temperature.
3. Chemical adsorption (chemisorption) of *Jatropha tanjorensis* leaf extract onto the mild steel surface has been proposed, based on an increase in inhibition efficiency with increase in temperature in addition to the E_a values of JTLE - H_2SO_4 medium being lower than that of the blank

4. The adsorption of *Jatropha tanjorensis* leaf extract onto mild steel surface obeyed the modified Langmuir adsorption isotherm.

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