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Mild steel corrosion inhibition in acidic medium by *Jatropha tanjorensis* stem bark extract

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Abstract
The inhibition of mild steel corrosion in sulphuric acid medium by *Jatropha tanjorensis* stem bark extract was studied by weight loss method. The data obtained reveal that the extract is a good inhibitor of mild steel corrosion in H_2SO_4 medium. The inhibition efficiency increased with increase in *Jatropha tanjorensis* stem bark extract concentration and temperature. The highest inhibition efficiency of 75.61% occurred at extract concentration of 4.0 g/L at 60 °C. The calculated thermodynamic parameters indicate that the adsorption process was endothermic and spontaneous. The adsorption of the stem bark extract on mild steel surface obeyed the Freundlich adsorption isotherm. Chemical adsorption has been proposed for the adsorption of *Jatropha tanjorensis* stem bark extract onto mild steel surface.

Keywords: *Jatropha tanjorensis,* corrosion inhibition, Freundlich isotherm, mild steel, chemisorption

1. Introduction
Corrosion takes a heavy toll on the economic resources of countries, as huge amounts of money which would have been used for national development are deployed in fighting it. The cost of corrosion has been estimated to be 2.5 trillion US dollars, amounting to 3.4% of the 2013 global GDP [1]. The need for the reduction of the corrosion rate of metals exposed to aggressive environments for the enhancement of the service life of metallic equipment is very imperative. The traditional inhibitors used in combating corrosion have been mainly inorganic and synthesised organic compounds [2-5]. Presently, the quest by researchers is for the formulation or extraction of eco-friendly inhibitors, as the use of traditional inhibitors is known to pose human health and environmental problems. Research efforts by scientists have yielded positive results with the extraction of eco-friendly inhibitors from natural products. Some special properties of this class of inhibitors include: biodegradability, renewability, cheapness and low toxicity. Some stem bark extracts reported as potential inhibitors of mild steel corrosion in acidic medium include: *Newbouldia laevis* [6], *Peltophorum ptetocarpum* [7], *Maranthes polyandra* [8], *Lannea nigritana* [9], *Eulychnia acida* Phil. [10] and *Microdesmis puberula* [11]. The search for more efficient eco-friendly inhibitors to combat the menace of metallic corrosion is ongoing.
Jatropha tanjorensis is a medicinal plant belonging to the family Euphorbiaceae. Previous studies [12] revealed that *Jatropha tanjorensis* leaf extract appreciably inhibited the corrosion of mild steel in acidic medium. The aim of this work is to assess the inhibitory effect of *Jatropha tanjorensis* stem bark extract on mild steel corrosion in sulphuric acid medium.

2. Materials and Method
2.1 Test materials
The chemical composition of the mild steel sheet used for this study was as follows (weight %)
C (0.12), Si (0.09), P (0.05), Mn (0.85), S (0.06), and Fe (98.83). The sheet was mechanically press-cut into 4 cm x 5 cm coupons. The coupons were polished to mirror finish using different grades of silicon carbide papers before degreasing in absolute ethanol, dipped in acetone and air-drying. Moisture-free desiccators were used in storing the coupons before use for corrosion studies.

2.2 Preparation of *Jatropha tanjorensis* stem bark extract
Fresh stem barks of *Jatropha tanjorensis* were obtained from a farm in Ikot Ekpene,

Akwa Ibom State, Nigeria. They were washed, cut into small pieces and air - dried at 30 °C for seven days. They were then ground to powder. *Jatropha tanjorensis* stem bark extract was obtained as described previously [12].

2.3 Weight loss method

Previously cleaned and weighed mild steel coupons were suspended with glass hooks and rods and completely immersed in 100 cm^3 of 1 M H_2SO_4 solution (blank) and in 100 cm^3 of 1 M H_2SO_4 solution containing 1.0 g/L - 4.0 g/L *Jatropha tanjorensis* stem bark extract (inhibitor) in open beakers. One mild steel coupon was contained in each beaker. The beakers were placed in 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 hours, scrubbed with bristle brush under running water, dipped in acetone and air-dried. The washed coupons were reweighed.

The corrosion rate (CR) of mild steel in the acid medium was calculated using the formula [13]:

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

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

The inhibition efficiency I (%) was calculated using equation (2) [14]:

$$I(\%) = \left(\frac{CR_0 - CR_1}{CR_0}\right) \times 100 \quad (2)$$

Where CR_0 and CR_1 are the corrosion rates of the mild steel coupons in the absence and in the presence of the extract, respectively.

3. Results and Discussion

3.1 Effect of *Jatropha tanjorensis* stem bark extracts concentration on inhibition efficiency

The effect of *Jatropha tanjorensis* stem bark extract concentration on the corrosion of mild steel in 1 M H_2SO_4 solution is depicted in Fig. 1. It is observed that at a given temperature the inhibition efficiency increases with increase in the extract concentration. The highest inhibition efficiency of 75.61% was obtained at 4.0 g/L extract concentration at 60 °C (Table 1). This reveals that *Jatropha tanjorensis* stem bark extract is a good inhibitor of mild steel corrosion in acidic medium.

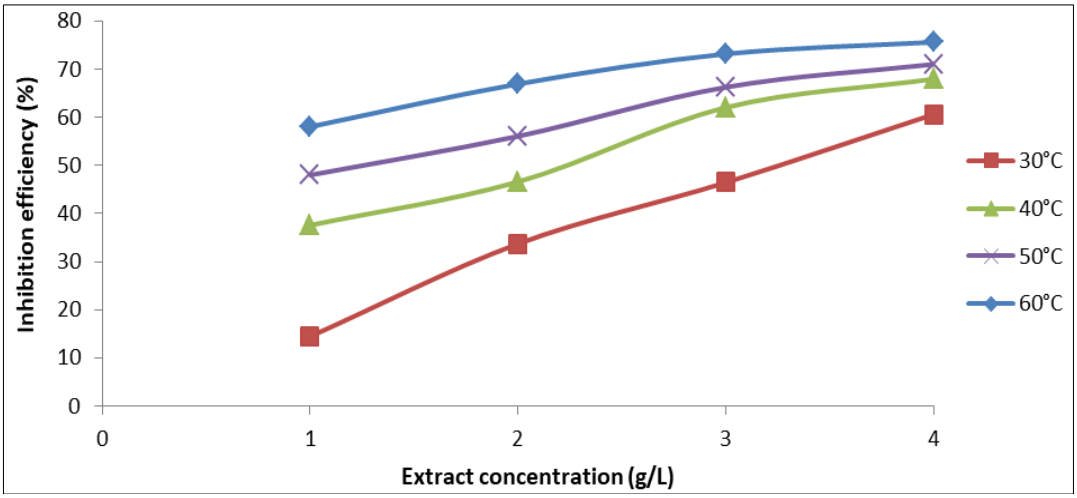

Fig 1: Effect of *Jatropha tanjorensis* stem bark extract concentration (g/L) on the inhibition efficiency (%) of mild steel corrosion in 1 M H_2SO_4 at different temperatures

Table 1: Weight loss data for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of different concentrations of *Jatropha tanjorensis* stem bark extract

Extract conc.	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
Blank	2.2063	3.1934	6.1688	9.7125	-	-	-	-
1.0 g/L	1.8875	1.9938	3.2063	4.0750	14.45	37.57	48.02	58.04
2.0 g/L	1.4625	1.7063	2.7125	3.2125	33.71	46.58	56.03	66.92
3.0 g/L	1.1813	1.2125	2.0813	2.6063	47.03	62.04	66.26	73.17
4.0 g/L	0.8688	1.0250	1.7875	2.3688	60.62	67.91	71.02	75.61

3.2 Effect of temperature on inhibition efficiency

Temperature had a profound effect on the inhibition efficiency of mild steel corrosion in 1 M H_2SO_4 solution containing *Jatropha tanjorensis* stem bark extract. The data presented in Table 1 reveal that as temperature increases, the inhibition efficiency also increases. This indicates that *Jatropha tanjorensis* stem bark extract is more effective as an inhibitor for mild steel corrosion at higher temperatures than at lower temperatures.

The activation energies (E_a) of mild steel corrosion in the absence and presence of *Jatropha tanjorensis* stem bark extract concentration were calculated using the alternative formulation of the Arrhenius equation [15]:

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

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

The E_a values presented in Table 2 were obtained from the gradients of ln CR vs. 1/T plot (Fig. 2). It is observed that the E_a of the blank (42.44 kJ mol^{-1}) is higher than that in the

presence of the extract. Lower E_a values in the presence of the extract compared to the blank indicate a chemical adsorption process while the reverse signifies a physical adsorption process [16 - 17]. Based on lower E_a values in the extract relative to the blank coupled with an increase of inhibition efficiency with increase in temperature, chemical adsorption of *Jatropha tanjorensis* stem bark extract onto mild steel surface has been proposed.

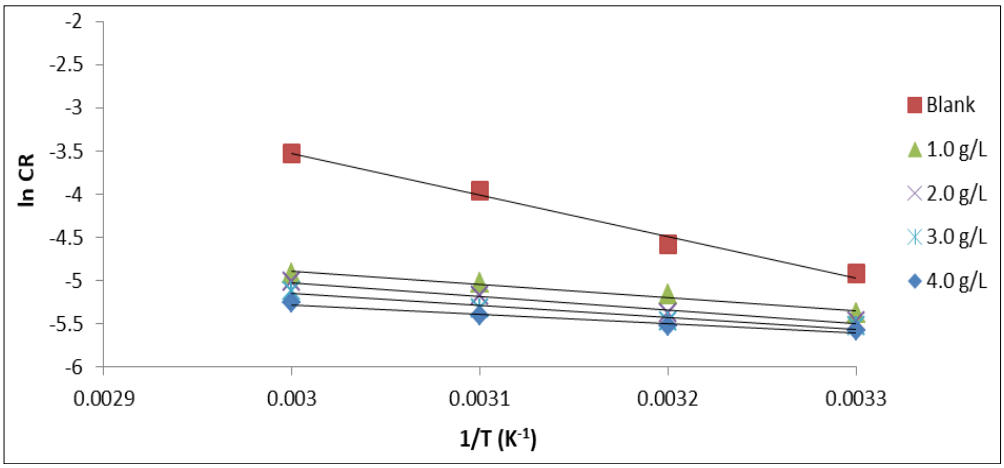

Fig 2: Arrhenius plot for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Jatropha tanjorensis* stem bark extract

The values of enthalpy of activation ($\Delta H°_{ads}$) and entropy of activation ($\Delta S°_{ads}$) presented in Table 2 were obtained using an alternative formulation of the transition state equation [18]:

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

Where CR is the corrosion rate, T is the absolute temperature, R is the universal gas constant, N is the Avogadro's number and h is the Planck's constant.

Values of $\Delta H°_{ads}$ and $\Delta S°_{ads}$ were calculated from the gradients ($-\Delta H°_{ads}/R$) and the intercepts [ln (R/Nh) + $\Delta S°_{ads}/R$] of ln (CR/T) vs. 1/T plots (Fig. 3), respectively, and presented in Table 2. The positive values of $\Delta H°_{ads}$ obtained reflect the endothermic nature of the corrosion inhibition process in the absence and presence of the extract. The values of $\Delta S°_{ads}$ presented in Table 2 are negative. The negative values of $\Delta S°_{ads}$ indicate a decrease in the disorderliness of the adsorption process [19]. In other words, the extract adhered strongly on the mild steel surface.

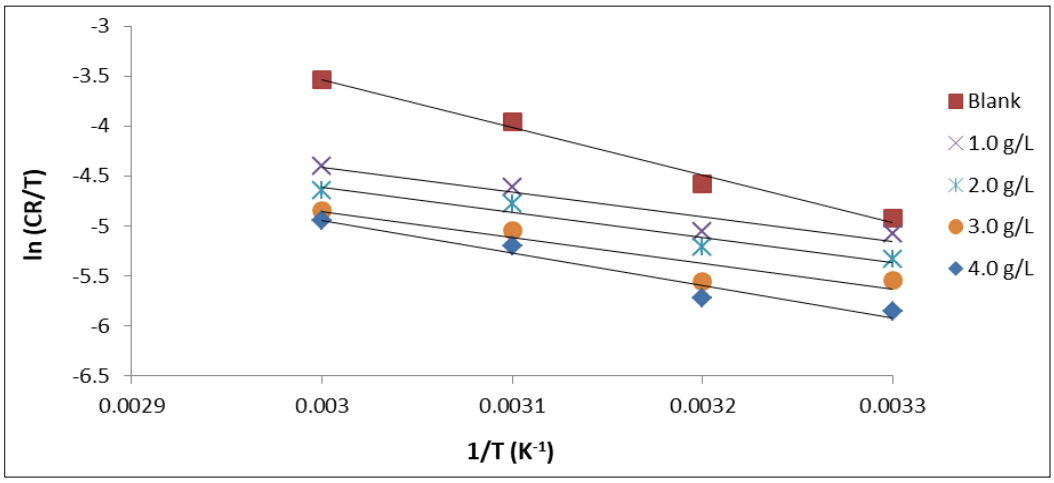

Fig 3: Transition state plot for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of *Jatropha tanjorensis* stem bark extract

Table 2: Thermodynamic parameters for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of *Jatropha tanjorensis* stem bark extract

Extract concentration	E_a (kJ mol^{-1})	$\Delta H°_{ads}$ (kJ mol^{-1})	$\Delta S°_{ads}$ (J K^{-1} mol^{-1})
1 M H_2SO_4 (Blank)	42.44	39.82	-107.43
1.0 g/L	23.15	20.53	-172.68
2.0 g/L	23.48	20.87	-173.32
3.0 g/L	24.23	21.62	-173.09
4.0 g/L	29.64	27.03	-157.55

3.3 Adsorption studies

The mode of interaction at the metal - inhibitor interface can be deduced by the adsorption isotherm obeyed by the adsorption process. Consequently, the experimental data were tested with several adsorption isotherms. The best fit for the adsorption of *Jatropha tanjorensis* stem bark extract on mild steel surface was obtained by the Freundlich adsorption isotherm defined as [20]:

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

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

Linear plots of log θ vs. log C (Fig. 4) with high coefficients of regression confirm that the Freundlich isotherm was obeyed. The values of some regression parameters obtained from the plot are presented in Table 3. Table 3 reveals that the equilibrium adsorption constant K_{ads} increased with increase in temperature. An increase in the value of K_{ads} as temperature is increased indicates that *Jatropha tanjorensis* stem bark extract adsorbed more strongly onto mild steel surface as temperature increases [19].

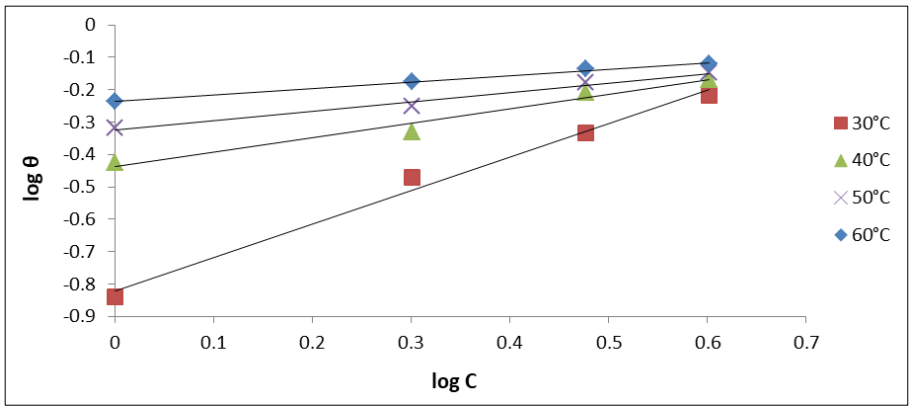

Fig 4: Freundlich isotherm plot for mild steel corrosion in 1 M H_2SO_4 solution containing *Jatropha tanjorensis* stem bark extract

The values of Gibb's free energy of the adsorption process ($\Delta G°_{ads}$), also presented in Table 3, were calculated using equation (6) [21 - 22]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G°_{ads}}{RT}\right) \quad (6)$$

Where R is the universal gas constant, T is the absolute temperature, K_{ads} is the equilibrium adsorption constant and 55.5 is the molar concentration of water in the solution. The negative values of $\Delta G°_{ads}$ obtained reveal the spontaneity of the corrosion inhibition process.

Table 3: Some parameters of the linear regression of Freundlich adsorption isotherm for mild steel corrosion in 1 M H_2SO_4 solution containing *Jatropha tanjorensis* stem bark extract

Temperature	R^2	n	log K_{ads}	K_{ads}	$\Delta G°_{ads}$ (kJ mol^{-1})
303 K	0.9902	1.03	-8.21 x 10^{-1}	1.51 x 10^{-1}	- 5.35
313 K	0.9695	0.44	-4.36 x 10^{-1}	3.66 x 10^{-1}	- 7.84
323 K	0.9829	0.29	-3.24 x 10^{-1}	4.74 x 10^{-1}	- 8.78
333 K	0.9929	0.20	-2.34 x 10^{-1}	5.83 x 10^{-1}	- 9.62

4. Conclusion

On the basis of this work, the following conclusions could be made:

1. *Jatropha tanjorensis* stem bark extract is a good inhibitor for mild steel corrosion in H_2SO_4 solution.
2. The inhibition efficiency increased with increase in extract concentration and temperature.
3. Chemical adsorption has been proposed for the adsorption of the extract on mild steel surface, since the inhibition efficiency increased with increase in temperature coupled with lower E_a values in the presence of the extract relative to the blank.
4. The positive values of $\Delta H°_{ads}$ and the negative values of $\Delta G°_{ads}$, respectively, reflect the endothermic and spontaneous nature of adsorption of *Jatropha tanjorensis* stem bark extract onto mild steel surface.
5. The adsorption of the extract onto mild steel surface obeyed the Freundlich adsorption isotherm.

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