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Inhibition studies of *Spondias mombin* L. in 0.1 HCl solution on mild steel and verification of a new temperature coefficient of inhibition efficiency equation for adsorption mechanism elucidation

T. O. Magu[1], **V. M. Bassey**[2], **B. E. Nyong**[3], **O. E. Obono**[4], **N. A. Nzeata-Ibe**[5] and **O. U. Akakuru**[6]

[1,4-6]Department of Pure and Applied Chemistry, University of Calabar, Calabar, Cross River State, Nigeria

[2,3]Department of Chemical Sciences, Cross River University of Technology, Calabar, Cross River State, Nigeria

E-mail address: tommy4life@yahoo.com

ABSTRACT

This research investigated the inhibition behavior of *Spondias mombin* leaf (SML) extracts in 0.1 M HCl solution on mild steel at various concentrations and temperatures. The result reveals that the inhibition efficiency of the extract on the mild steel sheet increases with increasing concentration of the extract and decreases with increase in temperature. Therefore, the adsorption mechanism of the extract on the mild steel surface is physical. Calculated Correlation Coefficient (R^2) values show that the process follows a Freundlich adsorption isotherm. The proposed temperature coefficient equation of adsorption mechanism was found to be appropriate.

***Keywords*:** Corrosion, Inhibitor, *Spondias mombin,* Freundlich adsorption isotherm, Inhibition coefficient

1. INTRODUCTION

Corrosion is a stepwise degradation of a material as a result of its interaction with the environment. It involves the deterioration of the mechanical properties of a material such as gradual reduction in tensile strength and surface area, etc. Corrosion may arise from the electrochemical oxidation of metals in reaction with an oxidant (i.e. oxygen) in the environment. This has become a major challenge in industries as many alloys and metals corrode on exposure to air and certain chemicals.

Corrosion deteriorates the appearance of a material which leads to reduced value of goods; contaminates fluids in vessels and pipes; block pipes with solid corrosion products; reduces the mechanical strength of a material leading to structural breakdown. According to corrosion due to acids is important and expensive problem in chemical industries as well as the petroleum refining industry. Due to corrosion, massive loss is sustained as a result of loss of production, inefficient fabrication, high cost of maintenance, and the cost of corrosion control chemicals as metal surfaces must be painted every few years.

Among the numerous approaches developed to control metallic corrosion, the use of inhibitors has proven to be the most practical and cost-effective means. Inhibitors are compounds which when added to a corroding specie, can effectively impede corrosion reaction by reducing the rate of attack on the material. Such a compound must be able to oxidize the metal, forming a passive layer on its surface. On the other hand, a molecule of an organic compound should possess a large structure, p bond, an active center or group, etc. These features give the molecule the ability to cover a large area of a metal surface with a firmly attached film. The use of naturally occurring substances of both plant and animal origin as inhibitors have been studied by various researchers.

In corrosion studies, equations like Gibbs' energy equation and Entropy calculation have been found useful. However, a new temperature coefficient of inhibition efficiency in physical adsorption mechanism has been introduced by various researchers. The new temperature coefficient (μ) is related to inhibition efficiency by the formula:

$$I_1 = \mu I_0 \Delta T + I_0 ------[1]$$

where I_0 and I_1 is the initial and final inhibition efficiency respectively. Some works on corrosion have been tested with this equation. Hence, this research is aimed at investigating the inhibition effect of *Spondias mombin* L. (SML) extract on the corrosion of mild steel using weight loss method as well as determining the applicability of the new temperature coefficient of inhibition efficiency equation in the corrosion inhibition process [1-9].

2. EXPERIMENTAL PROCEDURES

The mild steel sheet used for this work was obtained from System Metals Industries Limited, Calabar. The metal sheet was mechanically press-cut into coupons of dimension 4.0 cm by 4.0 cm. A small hole was made at the upper edge to aid insertion of glass hooks. Each coupon had a total surface area of 40.0 cm^2. The coupons were used as cut without further polishing. Prior to use, they were degreased by soaking in absolute ethanol (Aldrich Laboratories), dipped in acetone (BHD chemicals) and dried in air and then stored in moisture – free desiccator.

Spondias mombin L. (SML) was sourced locally. The leaves were washed, shredded, dried for 7 days and ground to fine powder. The powder was soaked in 90% ethanol for another seven days at room temperature. After filtration, the filtrates was evaporated at 40 °C to dryness, leaving a dark green solid material (plant extract) in the beaker. Extract concentrations of 1.0 g/L, 2.0 g/L, 4.0 g/L and 10.0 g/L in 0.1 M HCl solution respectively was used for weight loss studies at 30 – 60 °C.

Weight loss determination

Stage 1: previously weighed mild steel coupons were suspended by glass hooks and immersed in 0.1 M HCl solution in separate 100ml beakers kept at room temperature (30 °C) and in a thermostatic water bath maintained at 40 °C, 50 °C and 60 °C. The coupons were retrieved from the corroding solution after 5 hours, dipped into NaOH solution and washed severally with distilled water. The coupons were then dipped in acetone and dried in air before reweighing. The difference in weight was recorded as the weight loss. This stage served as the blank experiment.

Stage 2: different mild steel coupons of known weight were suspended each by glass hook and immersed in 100 ml of 0.1 M HCl containing different concentrations of the SML extracts (1.0 g/L, 2.0 g/L, 4.0 g/L and 10.0 g/L). Each coupon was retrieved from the HCl extract medium after 5 hours, washed and reweighed. The loss in weight was recorded. The weight loss was used to calculate the inhibition efficiency (%I) using the formula:

$$\%I = \left(\frac{W_o - W_1}{W_o}\right) X\,100 ------[2]$$

where $W_o - W_1$ are the final weight of the mild steel with and without inhibitors respectively.

Corrosion rate

The corrosion rate (mg/cm^2/hr) of mild steel was obtained using the equation:

$$CR = \frac{\Delta W}{A\,X\,t} ---------- [3]$$

where W is the weight loss of mild steel coupon (mg), A is the surface area of the mild steel (cm^2) and t is the immersion time (hr).

Surface coverage

$$\theta = \frac{inhibition\ efficiency\ (\%I)}{100} ------[4]$$

3. RESULT AND DISCUSSION

Weight loss, corrosion rate, and inhibition efficiency

The weight loss result for mild steel corrosion in both the blank and the SML extract medium at different temperature is presented in Table 1. The result revealed that the inhibition efficiency (% I) decreased as the temperature increased with the highest % I at 30 °C.

Likewise, the % I increased with an increase in the concentration of the extract medium with the highest efficiency occurring at 10.0 g/L. This result agrees with the report presented on melon and groundnut peel extracts as corrosion inhibitors for mild steel in HCl solution.

Figure 1a shows the variation of inhibition efficiency with temperature while Figure 1b shows the variation of inhibition efficiency with concentration of the extract. From the result, inhibition efficiency increased as the concentration of the inhibitor compared to the blank. Increase in inhibition efficiency with increase in inhibitor concentration is an indication that there is a strong interaction between the mild steel surface and the inhibitor.

The highest inhibition efficiency (Table 5) was 88.26 which occurred at 0 °C with SML concentration of 10 g/L. This result is smaller compared to 94.40% for groundnut peel extract and 92.64% for melon peel extract presented by However, the inhibition efficiency of SML (88.26%) is higher than 86.9% for pot marigold in 5 M HNO_3 solution presented and also higher than 62% for 0.5 g/L *Raphia hookeri gum* in 0.1 M H_2SO_4 at 30 °C.

Table 1. Weight loss result for mild steel immersed in 0.1M HCl solution containing various concentrations of SML extract at 30 – 60 °C

Temperature	System	Weight loss	Corrosion rate (CR)	Inhibition efficiency (%I)
30 °C	**Blank**	**0.0458**	**3.66**	**-**
	1.0 g/L	0.0104	0.83	77.44
	2.0 g/L	0.0092	0.72	80.32
	4.0 g/L	0.0083	0.66	82.01
	10.0 g/L	0.0054	0.43	88.26
40 °C	**Blank**	**0.1118**	**8.94**	**-**
	1.0 g/L	0.0353	2.82	68.42
	2.0 g/L	0.0313	2.50	72.08
	4.0 g/L	0.0261	2.09	76.65
	10.0 g/L	0.0208	1.66	81.43
50 °C	**Blank**	**0.2033**	**16.26**	**-**
	1.0 g/L	0.1028	8.22	49.41
	2.0 g/L	0.0908	7.26	55.32
	4.0 g/L	0.0769	6.15	62.19
	10.0 g/L	0.0603	4.82	70.37
60 °C	**Blank**	**0.4768**	**38.14**	**-**
	1.0 g/L	0.2553	20.42	46.45
	2.0 g/L	0.2205	17.64	53.76
	4.0 g/L	0.1729	13.83	63.74
	10.0 g/L	0.1733	13.86	64.19

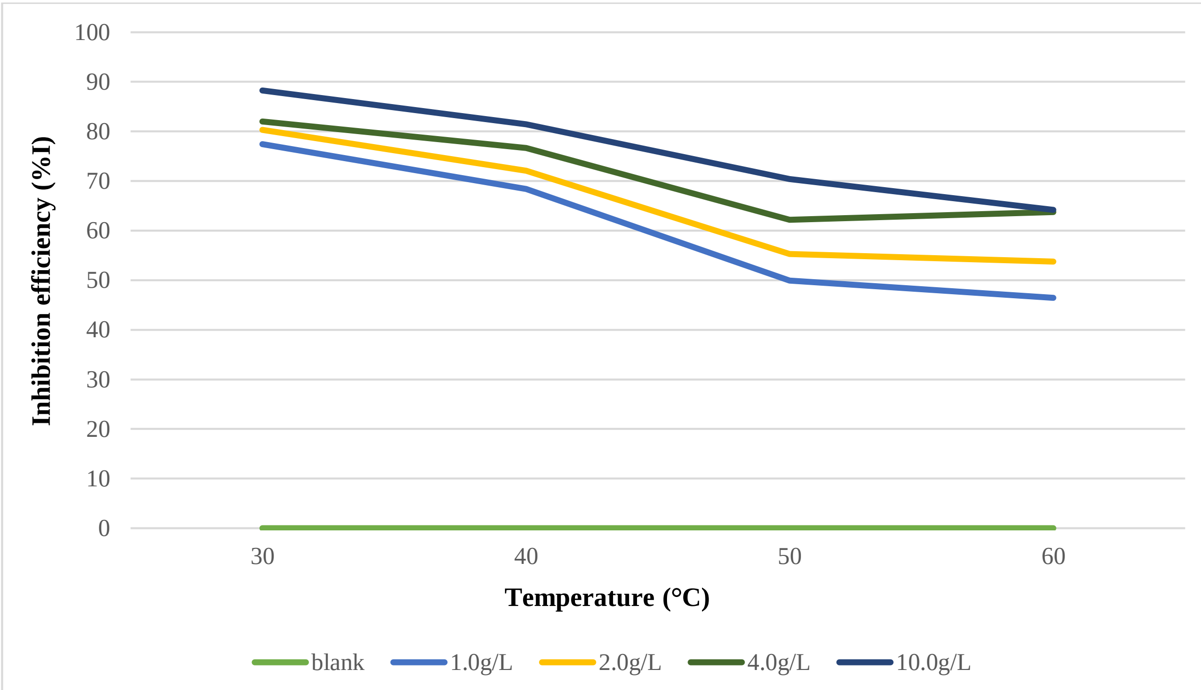

Figure 1a. Effect of temperature on inhibition efficiency of SML extract.

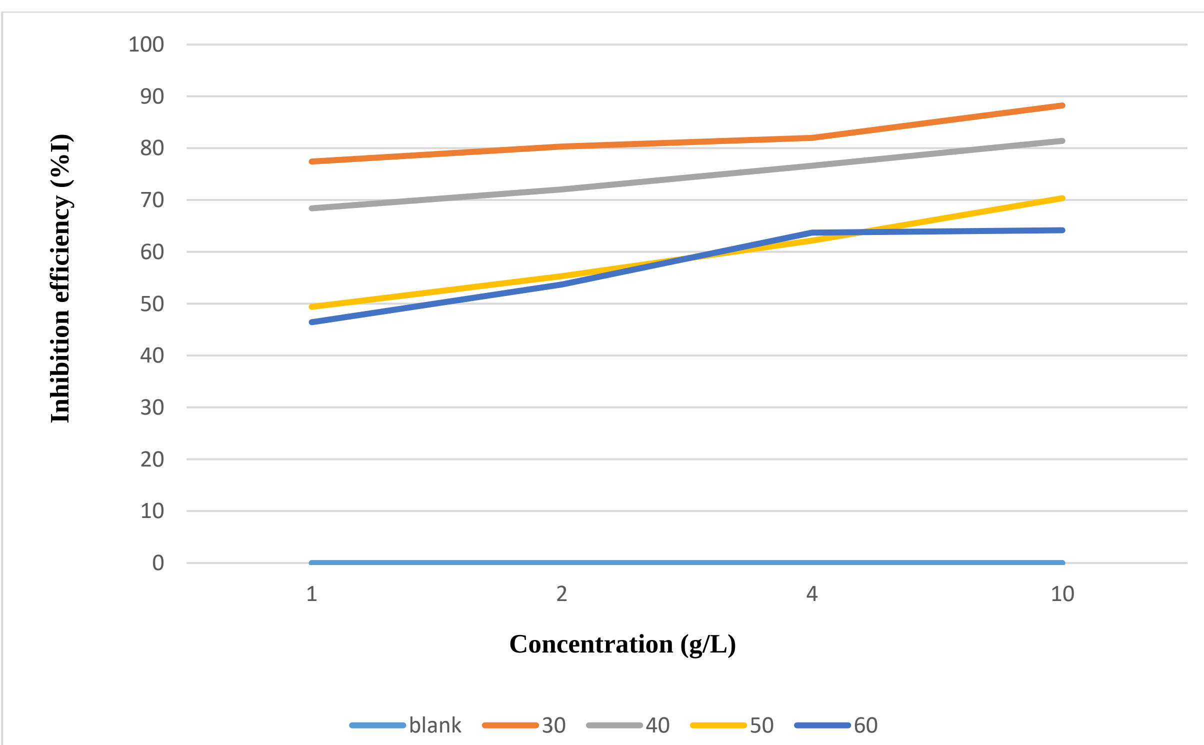

Figure 1b. Effect of concentration on inhibition efficiency of SML extract.

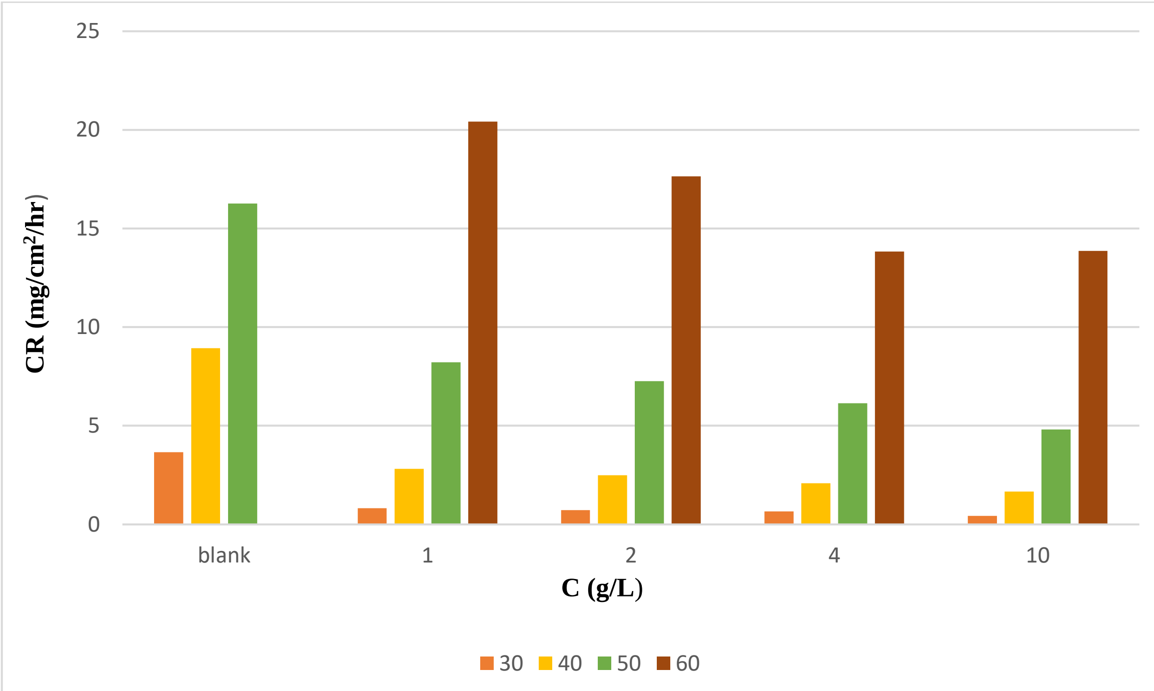

Figure 2. Corrosion rate in absence and presence of SML extract of different concentrations at different temperature

Table 2. Inhibition efficiency (%I), Corrosion rate (CR) and Surface coverage (θ) of the inhibitor at different concentrations for mild steel corrosion in 0.1M HCl solution for 5hrs using weight loss measurement.

System	**30 °C**			**40 °C**			**50 °C**			**60 °C**		
	CR	**%I**	θ	**CR**	**%I**	θ	**CR**	**%I**	θ	**CR**	**%I**	θ
Blank	**3.66**	**-**		**8.94**	**-**		**16.26**	**-**		**38.14**	**-**	
1.0 g/L	0.83	77.44	0.77	2.82	68.42	0.68	8.22	49.41	0.49	20.42	46.45	0.46
2.0 g/L	0.72	80.32	0.80	2.50	72.08	0.72	7.26	55.32	0.55	17.64	53.76	0.54
4.0 g/L	0.66	82.01	0.82	2.09	76.65	0.77	6.15	62.19	0.62	13.83	63.74	0.64
10.0 g/L	0.43	88.26	0.88	1.66	81.43	0.81	4.82	70.37	0.70	13.86	64.19	0.64

The activation energy (E_a) of the corrosion process in the absence and presence of the extracts was evaluated using the Arrhenius equation:

$$\ln CR = \frac{-E_a}{RT} + \ln A - - - - - - - - [5]$$

where R is the molar gas constant, T is the absolute temperature and A is the frequency factor.

If the Arrhenius equation is obeyed, a plot of ln CR vs. 1/T should be linear with a gradient of –Ea/R and an intercept of ln A. Figure 3 depicts an Arrhenius plot of ln CR against 1/T for SML extract in 0.1M HCl solution at different concentrations.

Table 3. Calculated values of thermodynamic parameters and μ values for the corrosion of mild steel in 0.1HCl solution with and without SML extract.

Extract concentration (g/L)	E_a (KJ mol^{-1})	ΔH_{ads}(KJ mol^{-1})	ΔS^0_{ads}(KJ mol^{-1})	μ
blank	0.64	0.61	-5.29	-
1.0	0.85	0.82	-6.99	-0.13
2.0	0.86	0.86	-7.13	-0.11
4.0	0.88	0.86	-7.18	-0.08
10	0.95	0.88	-7.65	-0.09

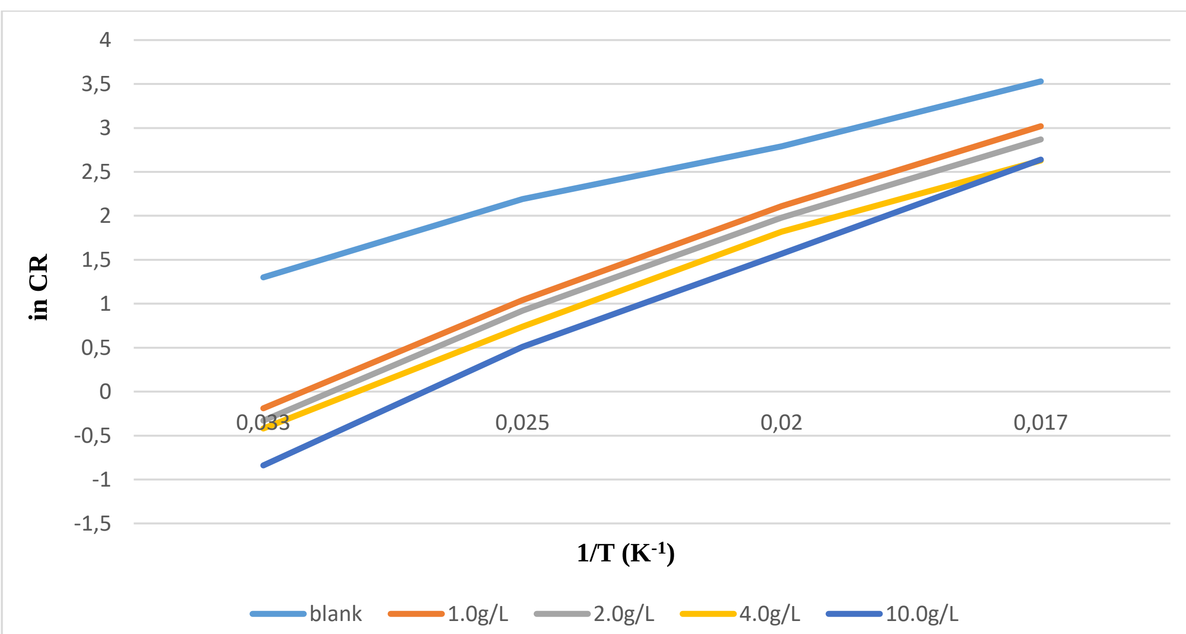

Figure 3. Arrhenius plot for mild steel corrosion in 0.1M HCl in the presence and absence of SML extract at different concentrations.

From the plot, satisfactory straight lines were obtained. The values of activation energy was obtained from the slopes of the linear plots and are presented in Table 3. It is clear that Ea values in the presence of SML extract at different concentration are higher than the blank values. The increase in apparent activation energy in the presence of the extract implies a physical adsorption while the reverse is usually attributed to chemical adsorption.

The higher activation energies mean a slow reaction and that the reaction rate is very sensitive to temperature. This conclusion is denoted by the decrease in inhibition efficiency with increasing temperature (Table 1). Similar result has been reported on *Raphia hookeri* gum as a potential eco-friendly inhibitor for mild steel in sulfuric acid. Moreover, the increase in activation energy is proportional to the inhibitor concentration, indicating that the energy barrier for the corrosion process is also increased (Table 3).

Table 4. Calculated linear regression parameters for the corrosion of mild steel in 0.1M HCl solution containing SML extracts.

TEMPERATURE	R^2	SLOPE	INTERCEPT	μ
30 °C	0.94	-11.19	±88.43	-0.13
40 °C	0.92	-9.64	±89.48	-0.12
50 °C	0.85	-6.92	±88.47	-0.11
60 °C	0.99	-8.32	±96.85	-0.09

The values of enthalpy of activation (ΔH^o_{ads}) and entropy of activation (ΔS^o_{ads}) were obtained from the transition state equation.

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S^0_{ads}}{R}\right)\exp\left(\frac{-\Delta H^0_{ads}}{RT}\right) - - - - - - - - - [5]$$

where E_a is the apparent activation energy, h is Planck's constant, N is Avogadro's number and R is the universal gas constant.

Adsorption isotherm and mechanism of adsorption

Adsorption isotherms are often used to characterize adsorption processes (Ituen et al, 2013). It is a common theory that the adsorption of the organic inhibitors at the metal interface is the first step in the mechanism of the inhibitors action. Attempts were made to fit (θ) values to the Frumkin, Freundlich, Temkin, and Langmuir isotherms and correlation coefficient (R^2) values were used to determine the best-fit isotherm. By far, the degree of surface coverage data fitted well into the Freundlich adsorption isotherm based on the R^2 values obtained. The fitting to the Freundlich isotherm is shown by plotting log C/ θ against log C (Figure 4).

According to this model, the surface coverage (θ) is related to the concentration (C) of the extracts according to the equation below:

$$\theta = n \log C + n \log K ------ [6]$$

where K is the adsorption-desorption equilibrium constant and n is a molecular attraction function determined by n= 1/f. The parameter K is related to the free energy of adsorption ΔG_{ads} according to the equation below:

$$\Delta G_{ads} = -RT \ln\ (55.5K) ------[7]$$

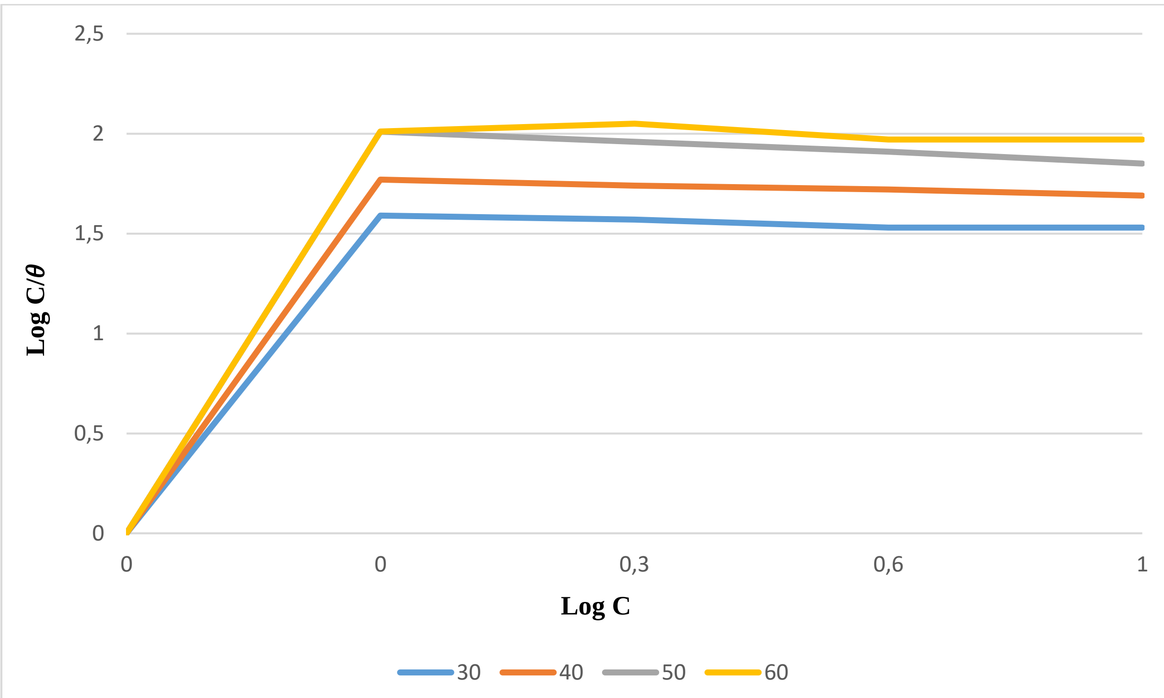

Figure 4. Freundlich adsorption isotherm for mild steel corrosion in 0.1M HCl in the presence of SML extracts at different concentration and temperature.

Figure 4 shows Freundlich adsorption isotherm for extract of SML while Table 4 shows the adsorption parameters deduced from the isotherm. Negative values were obtained for ΔG_{ads} indicating that the adsorption of the extracts unto the mild steel surface was spontaneous at all temperatures. It has been established that the values of ΔG_{ads} less than -40 KJ/mol are characterised as physical adsorption mechanism while those above -40KJ/mol are characterised by chemical adsorption. K_{ads} for leaves extract is related to the standard free energy of adsorption (ΔG_{ads}) by the formula:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}^{0}}{RT}\right) ------- [8]$$

where 55.5 is the molar concentration of water in the solution (mol/dm^3). The thermodynamic parameters for the adsorption of SML extracts are presented in Table 3.

Table 5. Parameters of linear regression of Freundlich adsorption isotherm, for corrosion of mild steel in 0.1M HCl solution containing SML extract.

Extract concentration (g/L)	Temperature (°C)	R^2	N	K_{ads}	ΔG_{ads}
1	30	0.99	0.018	0.739	-10.281
2	40	0.99	0.025	0.644	-9.602
4	50	0.96	0.050	0.438	-8.304
10	60	0.94	0.051	0.425	-7.923

The negative values of ΔG_{ads} for the plant extract indicates the spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface.

Where K_{ads} is the adsorption equilibrium constant. In this case, the curved plots were obtained at different temperatures indicating that the experimental results fit the Freundlich isotherm. The isotherm postulates that there is a relation between the concentrations of the absorbed molecules on the surface the adsorbent to the concentration of the extract with which it is in contact. The values of the correlation coefficients and the adsorption equilibrium constants are listed in Table 5. The correlation coefficients are quite good and indicate that the adsorption of the inhibitor (SML) on mild steel surface follows the Freundlich adsorption isotherm. K_{ads} denotes the strength between adsorbate and adsorbent. Large values of K_{ads} suggest more efficient adsorption and hence better inhibition efficiency. The values of K_{ads} decrease with increase in concentration and temperature (Table 5), suggesting that the inhibitor is physically adsorbed on the metal surface and desorption processes are enhanced by increase in temperature.

Application the New Temperature Coefficient of Inhibition Efficiency

The new temperature coefficient of inhibition is a different way of predicting adsorption mechanism. Table 5 presents a set of data obtained from the immersion of mild steel in 1M HCl solution containing various concentrations of SML extract.

Table 5. Thermometric and inhibition results for mild steel immersed in 0.1M HCl solution containing various concentrations of SML extract at different temperatures.

Concentration (g/L)	0 °C	10 °C	20 °C	30 °C
1.0	**77.44**	**68.42**	**49.41**	**47.45**
2.0	**80.32**	**72.08**	**55.32**	**53.76**
4.0	**82.01**	**76.65**	**62.19**	**63.74**
10.0	**88.26**	**81.43**	**70.37**	**64.19**

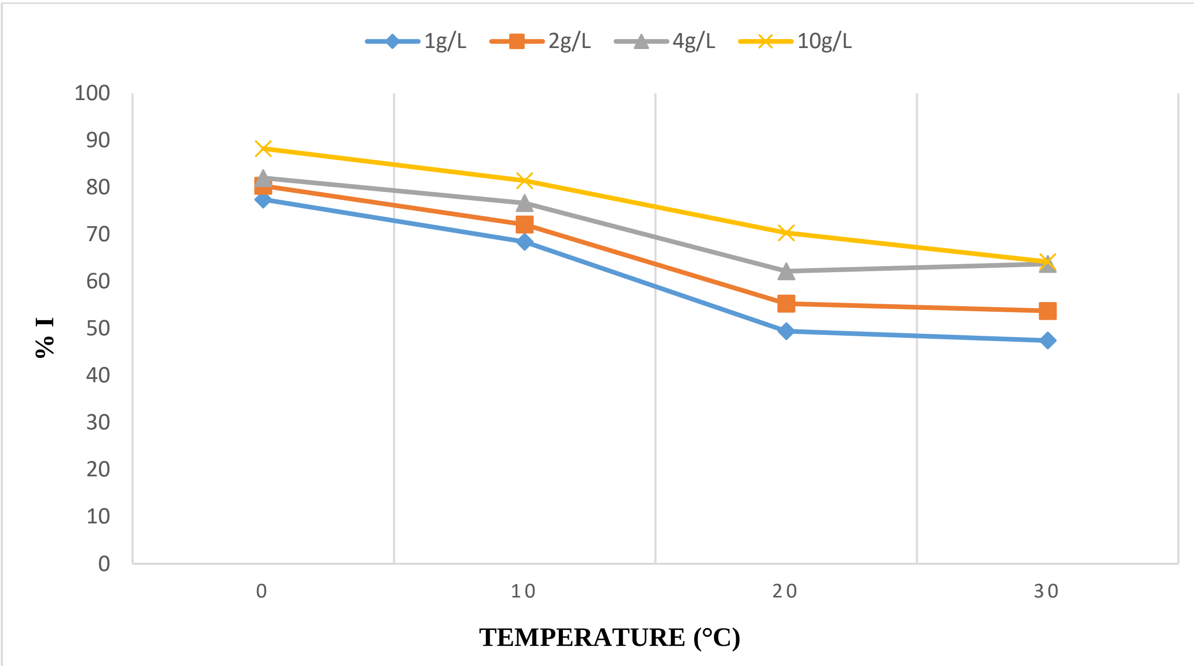

Figure 5. A plot of inhibition efficiency against change in temperature for SML extract

4. CONCLUSIONS

From the experimental results obtained from the study, it is concluded that increase in SML extract concentration increases inhibition efficiency and increase in temperature decreases inhibition efficiency. Therefore, for optimum result, corrosion rate of mild steel can be controlled using SML extract of 10 g/L at 10 °C.

However, further research should be made on roots, stem and bark extracts of *Spondias mombin* plant as well as other plants since they are non-toxic corrosion inhibitors. Also, structure of the active ingredient (i.e. compounds present in plant that are responsible for inhibiting corrosion) should be studied.

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