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COMPARATIVE ANALYSIS OF ADSORPTION AND CORROSION INHIBITIVE PROPERTIES OF ETHANOL EXTRACT OF DIALIUM

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ABSTRACT

In this study, the adsorption and corrosion inhibitive properties of ethanol extract of Dialium guineense leaves for mild steel in 0.5M HCl was studied using gravimetric method. The results obtained showed that the ethanol extract of Dialium guineense leave is a good adsorption inhibitor of Mild Steel in 0.5M HCl. The inhibition efficiency was found to increase with increase in the concentration of ethanol extract of Dialium guineense leave but decreased as the temperature increases. The inhibition efficiency increases up to a maximum of 92%. The kinetic study was found to follow pseudo first order reaction with high correlation. Thermodynamic consideration reveals that adsorption of ethanol extract of Dialium guineense leaves on mild steel surface is exothermic, spontaneous and fitted the Langmuir adsorption isotherm. The value of activation energy and Gibb's free energy obtained were within the range of limits expected for the mechanism of physical adsorption.

Keywords: *corrosion rate, Dialium guineense, inhibitor efficiency, Langmuir isotherm, mild steel*

INTRODUCTION

Corrosion is the deterioration of a metal due to its interaction with the environment such as water, acid, alkaline, air etc. Due to corrosion many useful properties of a metal such as malleability, ductility and electrical conductivity are lost. Hydrochloric and sulphuric acid are widely used acid pickling, industrial acid cleaning, acid descaling and oil-well cleaning (Selvi *et al.,* 2009). The use of inhibitors is one of the most practical methods for protection against corrosion. Synthetic organic compounds are widely used as corrosion inhibitors for the prevention of corrosion of many metals and alloys in various aggressive environments. Some of the synthetic organic compounds that show good anti-corrosive activity are highly toxic to cause hazards to both human and the environment during their application by Chinweuba (2014). The environmental hazards caused by the use of synthetic inhibitors had always been a global issue. Because of their hazardous nature, researchers focus their attention on developing cheap, non-toxic, biodegradable and environment friendly natural products of plant origin as corrosion inhibitors (Fouda *et al.*, 2014). However the use of plant extract as corrosion inhibitors has been reported to be environmental friendly, readily available, renewable and acceptable source of a wide range inhibitor by some researchers (Abdallah 2004; Abiola *et al*. 2007; Bendahou *et al*.,2006; Chetouani *et al* 2004; Rajendran *et al*. 2005; Sethuraman and Bothi Raja 2005). The antioxidant and antimicrobial activities of *Dialium guineense* leaves extract been reported (Ogu *et al* 2013). Therefore, this study aimed to investigate the inhibitive properties of *Dialium guineense* leaf extracts for corrosion of mild steel in 0.1MHCl using gravimetric techniques with and without the extract at 303K and 333K.

MATERIALS AND METHOD

PREPARATION OF PLANT EXTRACT (INHIBITOR)

Fresh leaves of *Dialium guineense* were obtained from Ahmadu Bello University botanical garden. The leaves were rinsed with distilled water to remove foreign particles. The leaves were later sun dried, ground and soaked in ethanol for 2 days. After 2 days, the sample was cooled and filtered. The filtrate was subjected to evaporation at 79^{o}C in order to leave the sample free from ethanol. The stock solution of the extract obtained were used in preparing different concentration of the extract by dissolving 0.1, 0.2, 0.3, 0.4, and 0.5g of the extract in 1dm^3 solution of 0.5M HCl respectively.

PREPARATION OF METAL SPECIMEN

Material used for the study was mild steel of composition (wt): Mn (0.6), P (0.36), C (0.15) and Si (0.03) and Fe (98.86). The sheet was cut into different coupons, each of dimensions 2×4cm. Each coupon was polished with emery papers of different grit sizes in order to obtain a smooth surface, degreased with ethanol, cleaned with acetone and allowed to dry in air before preserving in a desiccator.

GRAVIMETRIC MEASUREMENT

The mild steel coupon was accurately weighed and fully immersed in 100ml of corrosive solution in the absence and presence of the inhibitor in an open beaker. The beaker was covered with aluminum foil and maintained at 303K and different time interval. After every 24 hours, the corrosive product was removed, rinsed in distilled water, degreased

with ethanol, cleaned with acetone and allowed to dry in air before re-weighed. The experiment was repeated at 323K and the weight loss was determined in triplicate.

DETERMINATION OF WEIGHT LOSS

The weight loss was calculated using the formula below;

$$\text{Weight loss} = \frac{W_i - W_f}{W_i} \quad (1)$$

W_i = Initial weight of coupon before immersion

W_f = Final weight of coupon after immersion

DETERMINATION OF CORROSION RATE

The corrosion rate was calculated using the formula below;

$$\text{Corrosion rate (mm/y)} = \frac{87.6W}{DAT} \quad (2)$$

mm/y = millimetre per year

W = Weight loss (mg)

D = Density

A = Area of specimen (cm^2)

T = Time in hours

DETERMINATION OF INHIBITION EFFICIENCY

The inhibition efficiency was calculated using the formula below;

$$\%IE = \frac{CR_1 - CR_1}{CR_1} \times 100 \quad (3)$$

IE = Inhibition efficiency

CR_1 = Corrosion rate in the absence of inhibitor

CR_2 = Corrosion rate in the presence of inhibitor

DETERMINATION OF SURFACE COVERAGE

The surface coverage was calculated using the formula below;

$$\Theta = \frac{W_0 - W_1}{W_0} \quad (4)$$

Θ = surface coverage

W_0 = Weight loss in absence of inhibitor

W_1 = Weight loss in presence of inhibitor

RESULTS AND DISCUSION

Mild steel corrosion behavior in 0.5M HCl was investigated in the absence and presence of *Dialium guineense* extract using weight gravimetric method. The variation of weight loss with time for the corrosion of mild steel in 0.5M HCl

containing different concentration of ethanol extract of *Dialium guineense* leaves at 303k is shown in the figure 1 below;

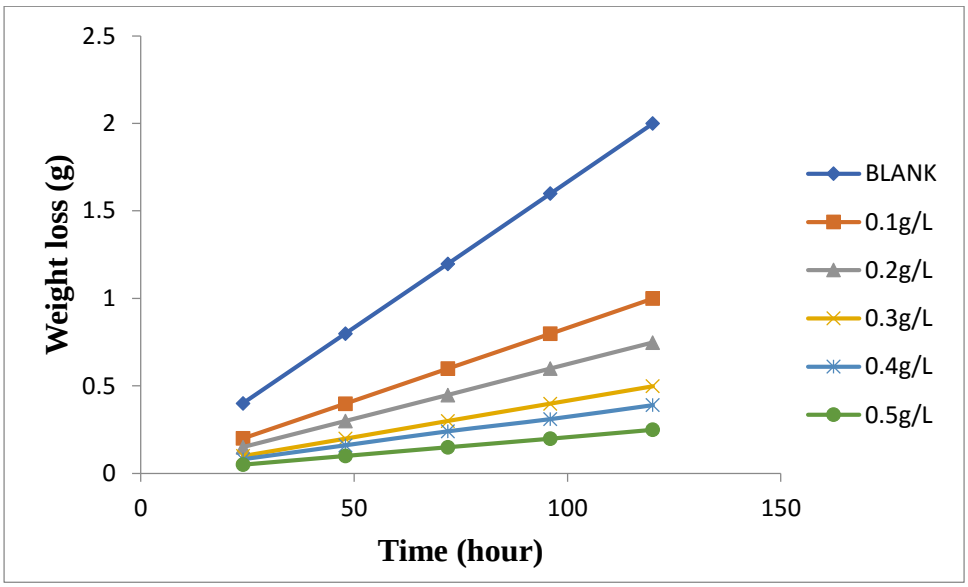

Figure 1: Variation of weight loss with time for the corrosion of mild steel in 0.5M HCl containing concentrations of ethanol extract of *Dialium guineense* leaves at 303k

From figure 1 above, the weight loss of mild steel increases with increase in immersion time but decreases as the concentration of the ethanol extract of *Dialium guineense* leaves increases. This implies that the extract retarded the corrosion of the mild steel in 0.5M HCl.

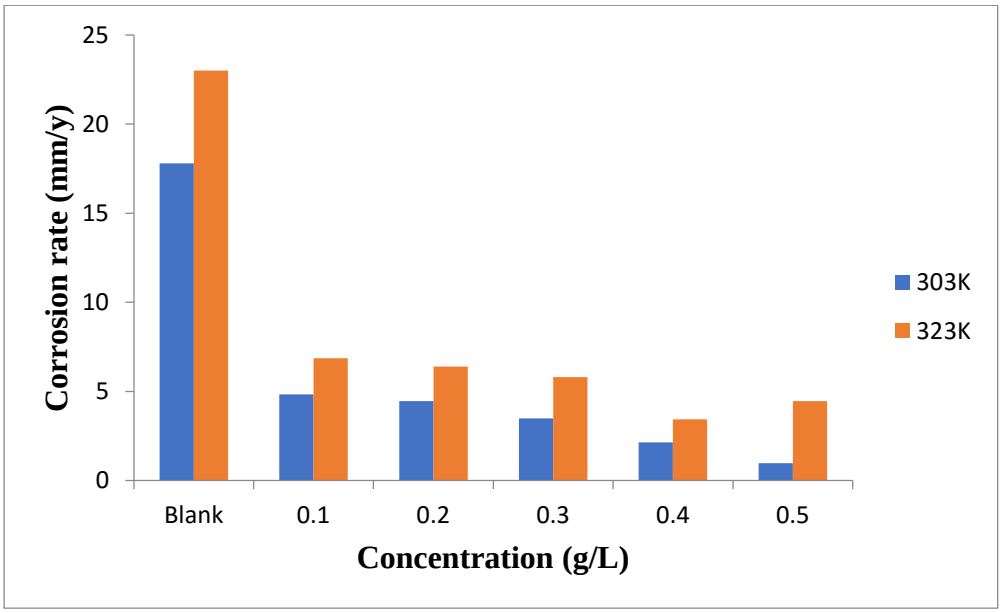

Figure 2: Variation of corrosion rate with concentration of ethanol extract of *Dialium guineense* leaves at 303K and 323K

The corrosion rate of mild steel in 0.5M HCl decreases with increase in concentration of the ethanol extract of Dialium guineense leaves as shown in figure 2. This shows that the extract inhibits the corrosion of the mild steel in 0.5M HCl. But the corrosion rate increases as the temperature increase due to the increase in the average kinetic energy of the reacting molecules. This is similar to the result in literature (Ebenso *et al.*,2015).

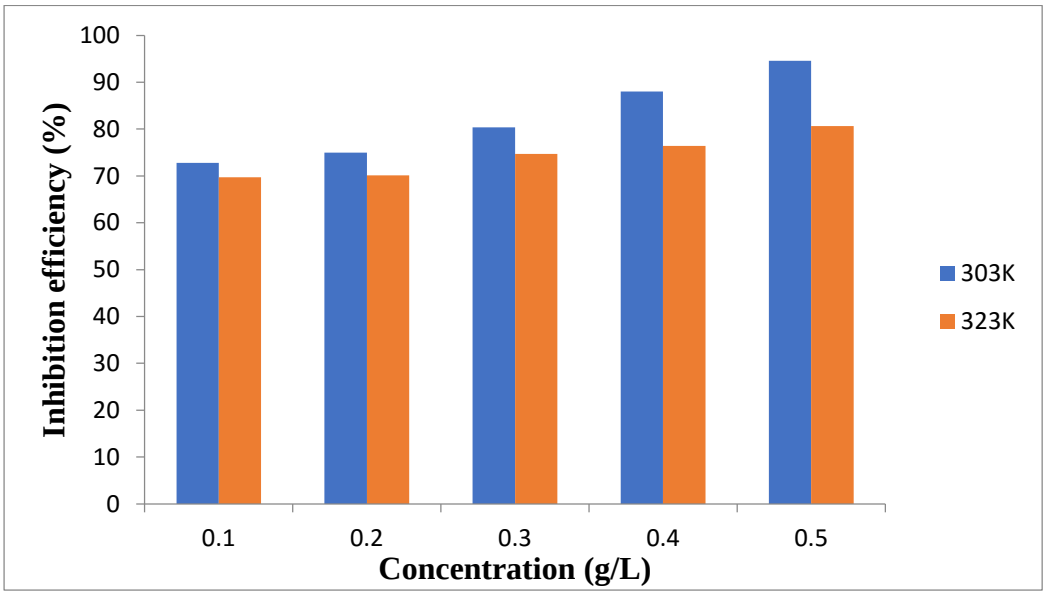

Figure 3: Variation of inhibition efficiency of ethanol extract of *Dialium guineense* leaves with concentration at 303K and 323K.

The significance difference between the value of inhibition efficiency of ethanol extract of *Dialium guineense* leaves with concentration at 303K and 323K suggest that the mechanism of adsorption of the inhibitor on the mild steel is by physical adsorption (Fouda *et al.,* 2012). For a physical adsorption mechanism, inhibition efficiency of an inhibitor decreases with temperature while for a chemical adsorption mechanism, values of inhibitor increase with temperature.

KINETIC CONSIDERATION

The kinetic study on the inhibition of the corrosion of mild steel in solution of 0.5 HCl by ethanol extract of *Dialium guineense* leaves of was found to follow pseudo first order reaction with the equation below;

$$K_1 = \frac{1}{t} ln\left(\frac{W_f}{W_i}\right) \quad (5)$$

Where;

W_f is the final weight of coupon after immersion, W_i is the initial weight of coupon before immersion, t is immersion time and K_1 is the rate constant for first order reaction. The consistency of K_1 table 1 below shows that the inhibition of the corrosion of mild steel in solution of 0.5 HCl by ethanol extract of *Dialium guineense* leaves is a first order reaction.

Table1: Rate constant for different concentration at different time interval

Time (hour)	K_1(hour^{-1})					
	Blank	**100mg/L**	**200mg/L**	**300mg/L**	**400mg/L**	**500mg/L**
24	0.00574	0.00215	0.00179	0.00150	0.000906	0.000418
48	0.00577	0.00225	0.00181	0.00151	0.000908	0.000425
72	0.00581	0.00241	0.00181	0.00151	0.000915	0.000435
96	0.00583	0.00245	0.00185	0.00153	0.000921	0.000441
120	0.00585	0.00256	0.00185	0.00154	0.000927	0.000452

Alternatively, K_1 can be determined using equation below;

$$\log W_f = \log W_i - \left(\frac{K_1 t}{2.303}\right) \quad (6)$$

Plot of log $W_{f\ versus}$ t yield a straight-line graph which is presented in Fig. 3.

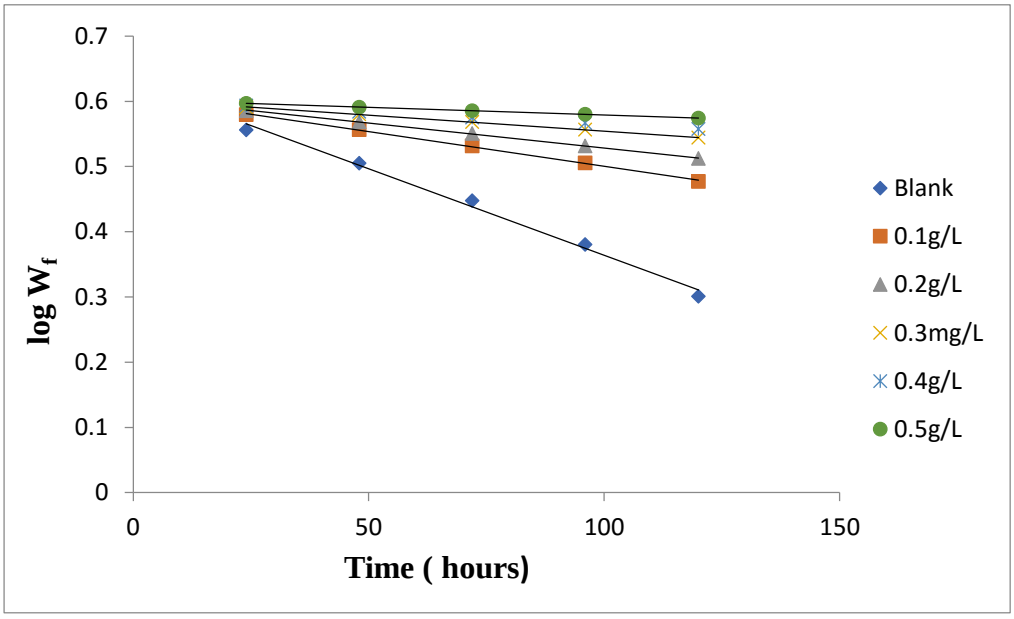

Figure 4: Variation of log W_f versus time for the corrosion of mild of mild steel in 0.1M HCl containing different concentration of ethanol extract of Dialium *guineense* leaves.

The half-life ($t_{1/2}$) was determined using the equation below;

$$t_{1/2} = \frac{0.693}{K_1} \quad (7)$$

Calculated value of K_1 and $t_{1/2}$ are presented in table 2. From the result obtained, it can be seen that ethanol extract of *Dialium guineense* leaves is a good corrosion inhibitor.

EFFECT OF TEMPERATURE

The effect of temperature on the corrosion of mild steel in HCl in the absence and presence of inhibitor was investigated using the logarithmic form of Arrhenius equation below;

$$\log\left(\frac{CR_2}{CR_1}\right) = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_1}\right) \quad (8)$$

CR_1 and CR_2 are the corrosion rate of mild steel at the temperature T_1 (303K) and T_2 (323K) respectively. Ea is the activation energy for the reaction and R is the molar gas constant (= 8.314KJ/mol). The activation energy calculated using equation (8) ranges from 14.66 to 63.43KJ/mol which was reported in table 2. The values are higher than the value of 10.66KJ/mol obtained for the blank which indicate that the extract retarded the corrosion of the mild steel in 0.5M HCl. The activation energies were also found to be lower than the threshold values of 80KJ/mol required for the mechanism of chemical adsorption. This implies that the adsorption of ethanol extract of *Dialium guineense* leaves on the mild steel surface obeys the mechanism of physical adsorption (Fouda et al., 2012).

Table 2: Kinetic parameters for the adsorption of ethanol extract of *Dialium guineense* leaves for the corrosion of mild steel.

Concentration (mg/L)	Slope	K_1(hour^{-1})	$t_{1/2}$(hour)	$t_{1/2}$(day)	E_a (KJ/mol)
Blank	-0.0026	0.00599	115.69	4.82	10.66
100	-0.0011	0.00253	273.4	11.4	14.56
200	-0.0008	0.00184	376.63	15.69	15.56
300	-0.0005	0.00152	455.92	19.00	21.19
400	-0.0004	0.000921	752.44	31.35	38.91
500	-0.0002	0.000461	1503.3	62.64	63.43

THERMODYNAMIC CONSIDERATION

The heat of adsorption (Q_{ads}) for ethanol extract of *Dialium guineense* leaves on mild steel was calculated using equation (9)

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left(\frac{T_1 \times T_2}{T_2 - T_1}\right) \quad (9)$$

Where Θ_1 and Θ_2 are the degree of surface coverage of the inhibitor at the temperature T_1 (303K) and T_2 (323K) and R is the molar gas constant. Calculated values of Q_{ads} were reported in table 3. These values are negative and ranges from -9.80 to -52.97KJ/mol indicating that the adsorption is exothermic.

The value of free energy of adsorption (ΔG_{ads}) for ethanol extract of *Dialium guineense* leaves were calculated using equation below; (Hamdy & El-Gendy, 2013)

$$\Delta G_{ads} = -2.303RT \log (55.5K_{ads}) \quad (10)$$

Where R is the molar gas constant, T is the temperature, 55.5 is the molar concentration of water (mL/L).

$$K_{ads} = \frac{\theta}{(1-\theta)\times C} \quad \text{(Noor, 2009)} \quad (11)$$

Calculated values of ΔG_{ads} were reported in table 3. These values range from 6.76 to 17.05 KJ/mol and tend to be more negative with increase in concentration of the inhibitor. These indicate that the adsorption of ethanol extract of *Dialium guineense* leaves on the mild steel surface is spontaneous and the strength of the adsorption increases with increase in concentration of the inhibitor. It is also a significant to note that values of $\Delta G_{ads\ less}$ negative than -40KJ/mol signifies the mechanism of physical adsorption.

Table3: Thermodynamic parameters for the adsorption for ethanol extract of *Dialium guineense* leaves for the corrosion of mild steel.

Concentration (g/L)	Q_{ads} **(KJ/mol)**	ΔG_{ads} **(KJ/mol)**	
		303K	323K
0.1	-9.80	-18.43	-6.76
0.2	-8.25	-16.95	-8.83
0.3	-13.85	-16.65	-10.58
0.4	-33.85	-17.45	-12.83
0.5	-52.97	-18.80	-17.05

ADSORTION ISOTHERM

Adsorption isotherms are very important in determining the corrosion reaction. The most frequent isotherms used are Langmuir, Freundlich, Temkim, Flory-Huggin, Frumkin, Parsons, Bockris-Swinkel and Dublin-Radushkevich. In this study, Langmuir isotherm was found to be suitable for the experimental findings and has been used to describe the adsorption characteristics of the inhibitor.

LANGMUIR ISOTHERM

Langmuir adsorption isotherm is expressed in the equation below;

$$\log (C/\Theta) = \log C - \log K \qquad (12)$$

Where K is the equilibrium constant of adsorption and Θ is the degree of surface coverage. Plot of C/Θ versus C yield a straight-line graph as shown in Fig.5. The values Kads was calculated from the intercept lines on the log (C/Θ) axis. Kads is related to the standard free energy of adsorption (ΔG_{ads}) by equation (6). The values of (ΔG_{ads}) for the inhibitor on the surface of mild steel are given in Table 4.

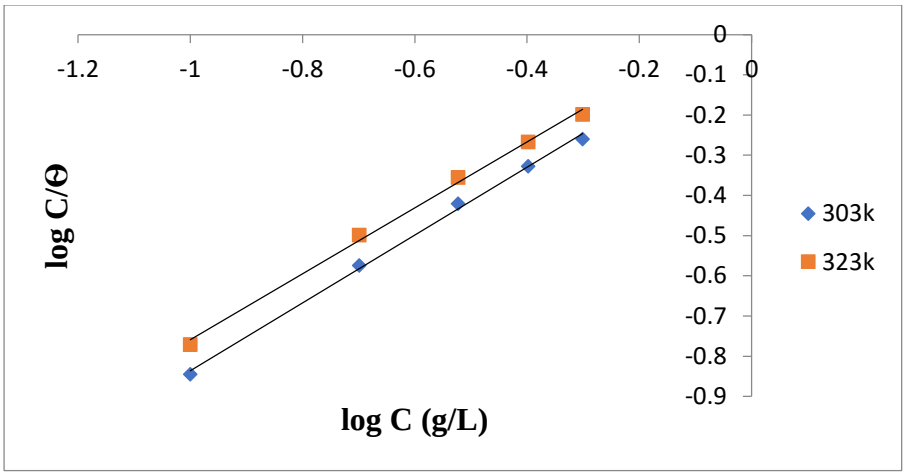

Figure 5: Langmuir isotherm for the adsorption of ethanol extract of *Dialium guineense* leaves on mild steel surface

The linear plot obtained indicates that the adsorption of the inhibitor is consistent with the assumption of Langmuir adsorption isotherm. The result obtained for the slope and R^2 are close to unity which is reported in table 4 indicates that Langmuir adsorption isotherm is valid for this system.

Table 4: Langmuir adsorption parameters and free energy of adsorption of ethanol extract *Dialium guineense* leaves on mild steel surface

	Slope	**R^2**	**Log K_{ads}**	**K_{ads}**	**ΔG_{ads} (KJ/mol)**
303K	0.8432	0.9977	-0.0071	0.9838	10.08
323K	0.8204	0.9968	-0.0611	0.8688	10.41

CONCLUSION

Ethanol extract of *Dialium guineense* leave is a good adsorption inhibitor of Mild Steel in 0.5M HCl. The adsorption characteristic of the inhibitor on mild steel surface is exothermic, spontaneous and obeys the mechanism of physical adsorption. The experimental data obtained fitted the Langmuir adsorption isotherm.

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