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Original scientific paper

Comparative analysis of adsorption and corrosion inhibitive properties of ethanol extract of *Dialium Guineense* leaves for mild steel in 0.5 M HCl

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Abstract

Adsorption and corrosion inhibitive properties of ethanol extract of Dialium guineense leaves for mild steel in 0.5 M HCl was studied using the gravimetric method. The results showed that the ethanol extract of Dialium guineense *leaves is a good corrosion inhibitor for mild steel in 0.5 M HCl. The inhibition efficiency was found to increase with increase in the concentration of ethanol extract of* Dialium guineense *leaves up to the maximum of 92 %, but at the same time it decreased as the temperature was increased. Corrosion inhibition by the extract of* Dialium guineense *leaves is carried out by adsorption mechanism with the kinetics of corrosion following the pseudo first order reaction with high correlation. Thermodynamic consideration revealed that adsorption of the ethanol extract of* Dialium guineense *leaves on mild steel surface is an exothermic and spontaneous process that fitted the Langmuir adsorption isotherm. The values of activation energy and Gibb's free energy were found 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 a 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. Metals are particularly prone to corrosion in hydrochloric and sulphuric acids that are in turn widely used for acid pickling, industrial acid cleaning, acid descaling and oil-well cleaning [1]. In such conditions, use of inhibitors became 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, however, highly toxic and can cause hazards to both human and the environment during their application [2]. The environmental hazards caused by the use of synthetic inhibitors have always been a global issue. In order to avoid these hazards, the researchers have focused their attention on developing cheap, non-toxic, biodegradable and environment friendly natural products of plant origin as corrosion inhibitors [3]. Plant extracts, including that of *Dialium guineense* leaves, have already been reported to be environmental friendly, readily available, renewable and acceptable source of a wide range corrosion inhibitors by some researchers [4–18]. The antioxidant and antimicrobial activities of *Dialium guineense* leaves extract has also been reported [19]. The present study aims to investigate inhibitive properties of *Dialium guineense* leaves extract for corrosion of mild steel at 303 K and 333 K, using the gravimetric technique and experiments performed with and without the extract present in 0.5 M HCl.

Experimental techniques

Preparation of plant extract (inhibitor)

Fresh leaves of *Dialium guineense* were obtained from Ahmadu Bello University botanical garden. The leaves were firstly rinsed with distilled water to remove foreign particles and then 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 °C in order to leave the sample free from ethanol. Different concentrations of the extract were prepared by dissolving 0.1, 0.2, 0.3, 0.4, and 0.5 g of the extract in 1dm^3 of 0.5 M HCl, respectively.

Preparation of metal specimen

Material used for the study was a mild steel sheet of the following composition (wt): Mn (0.6), P (0.36), C (0.15) and Si (0.03) and Fe (98.86). The sheet was cut into coupons, each of dimensions 2×4×0.1 cm. 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 its preserving in a desiccator.

Gravimetric measurements

The mild steel coupon was accurately weighed and fully immersed in 100 ml of corrosive solution (without or with the inhibitor present in 0.5 M HCl) in an open beaker. The beaker was covered with the aluminum foil and maintained at 303 K for different time intervals. After every 24 hours, the corrosive product was removed from the coupon which was further rinsed in distilled water, degreased with ethanol, cleaned with acetone and allowed to dry in air before the re-weight. The experiment was repeated at 323 K and the weight loss was determined in triplicate.

Determination of weight loss

The weight loss (W) was calculated using the following formula:

$$W = W_i - W_f \tag{1}$$

where W_i is the initial weight in g of the coupon before immersion, while W_f is the final weight in g of coupon after immersion.

Determination of corrosion rate

The corrosion rate (CR) was calculated using the following formula:

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$$\text{CR, mm year}^{-1} = \frac{87.6W}{DAt} \tag{2}$$

where W is the weight loss in g, D is density in g cm^{-3}, A is the area of specimen in cm^2 and t is time of immersion in hours.

Determination of inhibition efficiency

The inhibition efficiency (IE) was calculated using the following formula:

$$\text{IE, \%} = \frac{\text{CR}_1 - \text{CR}_2}{\text{CR}_1} 100 \tag{3}$$

where IE is inhibition efficiency, CR_1 is corrosion rate in the absence of inhibitor, while CR_2 is corrosion rate in the presence of inhibitor.

Determination of surface coverage

The surface coverage (θ) was calculated using the following formula:

$$\theta = \frac{W_0 - W_1}{W_0} \tag{4}$$

where W_0 is the weight loss in absence of inhibitor, while W_1 is the weight loss in presence of inhibitor.

Results and discussion

Mild steel corrosion behavior was investigated in the absence and presence of *Dialium guineense* extract in 0.5 M HCl, using the gravimetric method. The variation of weight loss with immersion time for the corrosion of mild steel in 0.5 M HCl containing different concentrations of ethanol extract of *Dialium guineense* leaves at 303 K is shown in Figure 1.

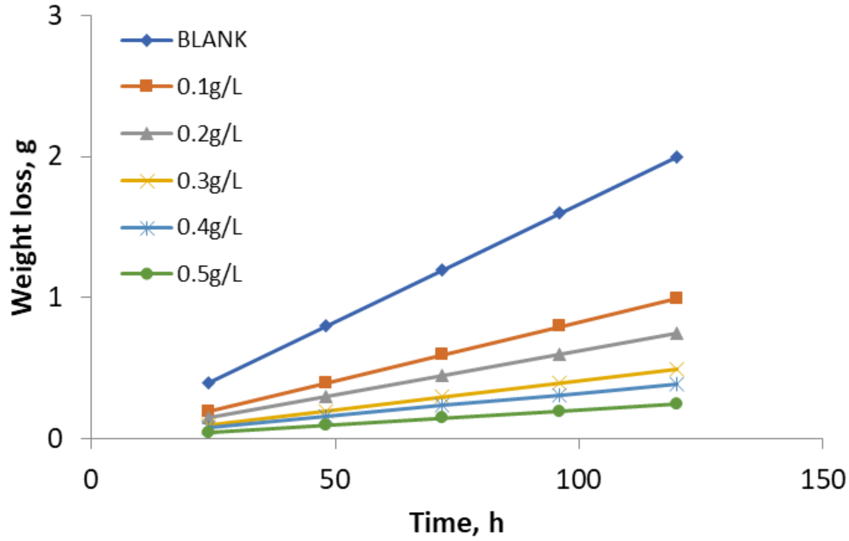

***Figure 1**: Variation of weight loss with immersion time for corrosion of mild steel in 0.5 M HCl containing different concentrations of ethanol extract of* Dialium guineense *leaves at 303 K.*

It is seen in Figure 1 that 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 presence of the extract retards corrosion of the mild steel in 0.5 M HCl. As shown in Figure 2, the corrosion rate of mild steel in 0.5 M HCl calculated by eq. (2), decreases with increase in the concentration of the ethanol extract of *Dialium guineense* leaves, suggesting again that the extract inhibits corrosion of the mild steel in 0.5 M HCl. Also, corrosion rates at all concentrations of inhibitor increase with the temperature increase, what is due to the increase in the average kinetic energy of the reacting molecule and similar to the already reported results [20,21].

Variations of the inhibition efficiency calculated by eq. (3) for different concentrations of the ethanol extract of *Dialium guineense* leaves at 303 K and 323 K are presented in Figure 3. Significant differences between inhibition efficiency of the ethanol extract of *Dialium guineense* leaves determined at 303 K and 323 K for each concentration of the inhibitor, suggest that the mechanism of adsorption of the inhibitor on the mild steel is physical adsorption [22]. For a physical adsorption mechanism, inhibition efficiency of an inhibitor decreases with temperature while for a chemical adsorption mechanism, inhibition efficiency increases with rise of the temperature.

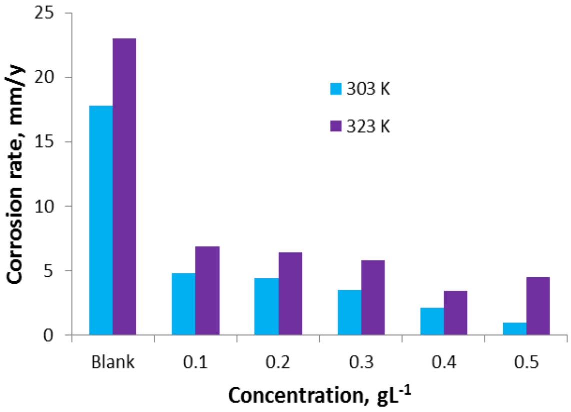

Figure 2. *Variation of corrosion rate with concentration of ethanol extract of* Dialium guineense *leaves at 303 K and 323 K.*

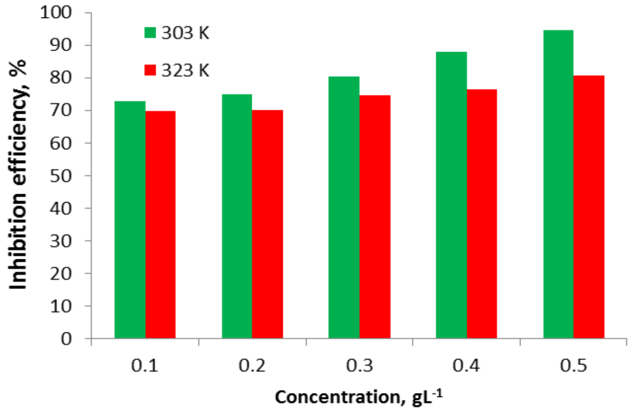

Figure 3: *Variation of inhibition efficiency of ethanol extract of Dialium guineense leaves with concentration at 303 K and 323 K.*

Kinetic consideration

The kinetic study on the corrosion inhibition of the corrosion of mild steel in solution of 0.5 HCl by ethanol extract of *Dialium guineense* leaves suggests a run of the pseudo first order reaction according to the following rate constant equation:

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

In eq. (5), K_1 is the rate constant for the first order reaction, W_f is the final weight of coupon after immersion, W_i is the initial weight of coupon before immersion, while t is immersion time.

The consistency of K_1 values listed in Table 1 suggests that corrosion of mild steel in either blank solution of 0.5 HCl or with different concentrations of the ethanol extract of *Dialium guineense* leaves is the first order reaction.

Table1. *Rate constant of corrosion for different concentrations of* Dialium guineense *leaves extract at different time intervals*

Time, h	K_1 / h^{-1}					
	Concentrations of *Dialium guineense* leaves extract, mg L^{-1}					
	0	100	200	300	400	500
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 graphically using eq. (5) written in the following form:

$$\log W_\mathrm{f} = \log W_\mathrm{i} - \frac{K_1 t}{2.303} \tag{6}$$

Plot of log W_f versus t yields a straight-line graph which is for different concentrations of the extract of *Dialium guineense* leaves presented in Figure 4.

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

$$t_{1/2} = \frac{0.693}{K_1} \tag{7}$$

Calculated values 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.

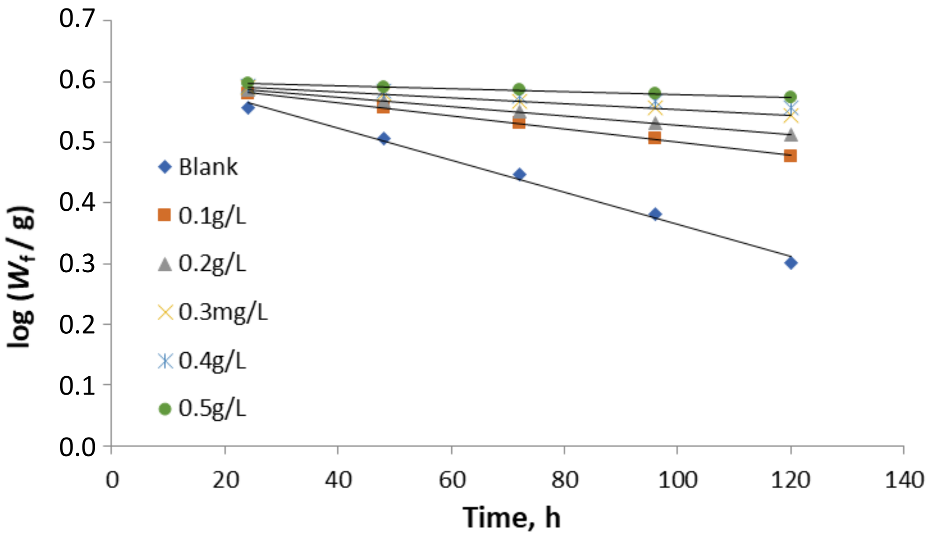

Figure 4. *Variation of log* W_f vs. *immersion time for the corrosion of mild steel in 0.1 M HCl containing different concentrations of ethanol extract of* Dialium guineense *leaves.*

Table 2. *Kinetic parameters of mild steel corrosion inhibited by ethanol extract of Dialium guineense leaves.*

Concentration, mg L^{-1}	Slope	K_1 / h^{-1}	$t_{1/2}$ / h	E_a / kJ mol^{-1}
Blank	-0.0026	0.00599	115.69	10.66
100	-0.0011	0.00253	273.4	14.56
200	-0.0008	0.00184	376.63	15.56
300	-0.0005	0.00152	455.92	21.19
400	-0.0004	0.000921	752.44	38.91
500	-0.0002	0.000461	1503.3	63.43

Effect of temperature

The effect of temperature on the corrosion of mild steel in 0.5 M HCl in absence and presence of inhibitor was investigated using the logarithmic form of the Arrhenius equation:

$$\log\left(\frac{CR_2}{CR_1}\right) = \frac{E_\mathrm{a}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8}$$

In eq. (8), CR_1 and CR_2 are corrosion rates of mild steel at absolute temperatures T_1 (303 K) and T_2 (323 K), respectively. E_a is the activation energy for the reaction and R is the molar gas constant 8.314 J K^{-1} mol^{-1}). As can be seen in Table 2, the values of activation energy calculated by eq. (8) range from 14.66 to 63.43 kJ mol^{-1}. These values are found higher than the value of 10.66 kJ mol^{-1} obtained for the blank solution, which indicates an inhibition of corrosion of the mild steel in

0.5 M HCl, caused by presence of the extract. The activation energies are also found lower than the threshold values of 80 kJ mol^{-1} required for the mechanism of chemical adsorption. This implies that adsorption of ethanol extract of *Dialium guineense* leaves on the mild steel surface obeys the mechanism of physical adsorption [22].

Thermodynamic consideration

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

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right]\frac{T_1T_2}{T_2-T_1} \tag{9}$$

where θ_1 and θ_2 are the degree of surface coverage of the inhibitor at the absolute temperature T_1 (303 K) and T_2 (323 K), respectively and R is the molar gas constant. The values of Q_{ads} calculated using eq. (9) are reported in Table 3. These values are negative and range from –9.80 to –52.97 kJ mol^{-1}, indicating that adsorption is an exothermic process.

The values of free energy of adsorption (ΔG_{ads}) for the ethanol extract of *Dialium guineense* leaves are calculated using the following equation [23]:

$$\Delta G_{ads} = -2.303\,R\,T\log(55.5K_{ads}) \tag{10}$$

where R is the molar gas constant, T is absolute temperature, 55.5 is the molar concentration of water in mol L^{-1} and K_{ads} is the equilibrium constant of adsorption defined as [24]:

$$K_{ads} = \frac{\theta}{(1-\theta)C} \tag{11}$$

Values of ΔG_{ads} calculated using eq. (10-11) are reported in Table 3. The values of ΔG_{ads} range from –6.76 to –17.05 kJ mol^{-1} and tend to be more negative with rise in the concentration of the inhibitor. This indicates that adsorption of the ethanol extract of *Dialium guineense* leaves on the mild steel surface is spontaneous and the strength of adsorption increases with increase in concentration of the inhibitor. It is also a significant to note that values of ΔG_{ads} that are less negative than -40 kJ mol^{-1} suggest the mechanism of physical adsorption.

Table 3. *Thermodynamic parameters for adsorption of ethanol extract of Dialium guineense leaves on mild steel.*

Concentration, g L^{-1}	Q_{ads} / kJ mol^{-1}	ΔG_{ads} / kJ mol^{-1}	
		303 K	323 K
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

Adsorption isotherm

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

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Langmuir isotherm

Langmuir adsorption isotherm is expressed by the following equation:

$$\log (C/\theta) = \log C + \log (1/K_{ads}) \tag{12}$$

where K_{ads} is the equilibrium constant of adsorption, C is bulk concentration of adsorbing (inhibitor) species and θ is the degree of surface coverage. As shown in Figure 5, a plot of log C/θ versus log C yields a straight-line graph.

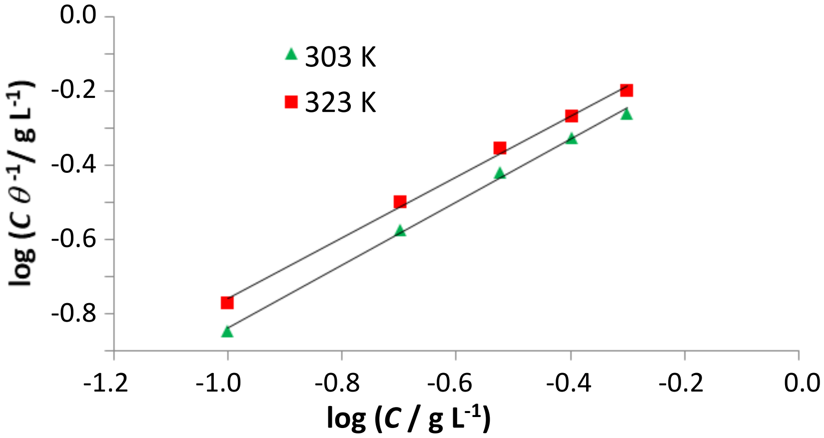

Figure 5. *Langmuir isotherm for the adsorption of ethanol extract of* Dialium guineense *leaves on mild steel surface*

The linear plots presented in Figure 5 having slopes and correlation coefficients (R^2) listed in Table 4, indicate that adsorption of the inhibitor is highly consistent with the Langmuir adsorption isotherm. The values of K_{ads} at two temperatures were determined from the intercept lines on the log (C/θ) axis and listed in Table 4, together with ΔG_{ads} values for the inhibitor adsorption on the surface of mild steel, calculated using eq. (10).

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

T / K	Slope	R^2	log K_{ads}	K_{ads}	ΔG_{ads} / kJ mol^{-1}
303	0.8432	0.9977	-0.0071	0.9838	-10.08
323	0.8204	0.9968	-0.0611	0.8688	-10.41

Conclusion

Ethanol extract of *Dialium guineense* leaves effectively inhibited corrosion of mild steel in 0.5 M HCl. Inhibition efficiency of the extract increased with increase of concentration of *Dialium guineense* leaves but decrease with rise in the temperature. This suggests that corrosion inhibition can be attributed to the physisorption mechanism. The mechanism of physisorption was further confirmed by examining the values of apparent activation energies and heat of adsorption. The adsorption of the ethanol extract of *Dialium guineense* leaves inhibitor on mild steel surface is an exothermic and spontaneous process that fits the Langmuir adsorption isotherm.

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