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Research Article

The Behaviour of *Moraceae ficus glumosa delile* as a Corrosion Inhibitor for Zinc in H_2SO_4

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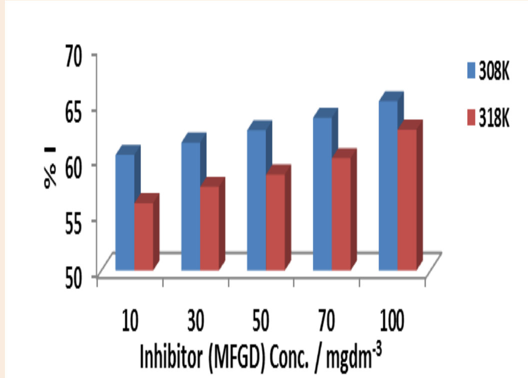
Abstract

Moraceae ficus glumosa delile (MFGD) leaf extract was tested on zinc metal in 0.50M H_2SO_4 solution as a new corrosion inhibitor using mass loss measurements. The adsorption of MFGD on the zinc surface in H_2SO_4 solution follows a Langmuir and Frumkin's adsorption isotherms. The effect of temperature indicated that the corrosion rate and the inhibitor efficiency (%I) are temperature dependent in the range of 308K and 318K. Increase in temperature increased the corrosion rate but decreased the inhibitor efficiency (%I) in the absence and presence of the inhibitor. The kinetic data obtained indicates that the adsorption follows a first order type of reaction. Physisorption has been proposed for the inhibitor.



Keywords: Corrosion inhibitor, *Moraceae ficus glumosa delile*, Zinc metal, Langmuir model, Frumkin's isotherm

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Introduction

Corrosion is a reaction in which metals are attacked by some substances in its environment become changed an unwanted compound. Corrosion can also be defined as a chemical reaction taking place at the surface of metals, which can be converted into a chemical compounds [1]. Corrosion causes great damage to building, bridges, cars, ships, machines etc. [2]. Corrosion cost according to El-Meligi [3], should be drawn between direct and indirect costs as it damages everything from cars, home appliances, bridges e.t.c.

Zinc is a reactive metal. It reacts with acids to produce zinc ions (Zn^{2+}) and hydrogen gas. Zinc is a bluish - white solid with lust relative density of 7.1, malleable and ductile between 100 – 150^{o}c, high tensile strength, melting point of 149^{o}C and good conductor of heat and electricity [4]. The most important use of zinc is in providing a protective coating for the metals. Although zinc is an active metal, it forms an adherent oxide coat that protects the zinc from further oxidation by air. Galvanized steel is made by dipping steel sheets in molten zinc [5].

When metallic zinc is exposed to water, oxygen and other agents, metallic corrosion results loss of structural integrity or degradation in surface appearance is observed [3]. It also leads to the reduction of the metal thickness, loss of mechanical strength and structural failure or break down.The use of corrosion inhibitors is one of the most effective methods of protecting the surface of metal/alloy against corrosion in acid/alkaline environments. Inhibition of zinc corrosion using various organic, inorganic compounds, dyes and plants extracts has therefore received wide spread attention [6-8].

Moraceae ficus glumosa delile (also called Gaḿjì or Ganyi in Hausa) is a robust tree or shrub, 12 – 15m high, with a 2 – 3m high, squat bole up to 2m in diameter. The tree is smooth, becoming scaly when old, yellowish – grey to brown, with pink or red sash executing latex. It in most parts of Northern Nigeria, Senegal, Cameroon, Ethiopia, Eastern and Southern Africa and Yemen [9].

Corrosion inhibitors are substances that when added in small amounts to a corrosive aqueous environment reduces the rate of metal wastage. Most inhibitors are organic compounds containing hetero atoms (N, O, and S) in their structures. Most of the synthetic compounds (organic, inorganic, coatings etc.) used as inhibitors are very expensive and equally source of several health hazards[10]. Their toxic characteristics limit the field of their application. It has become necessary therefore to find less expensive and non – hazardous inhibitors for the protection of materials/alloys against corrosion.

From available literature, the use of *Moraceae ficus glumosa delile* (MFGD) leaf extracts has not been reported as a corrosion inhibitor. This study is therefore aimed at evaluating adsorption characteristics and inhibitive properties of *Moraceae ficus glumosa delile* leaf extracts as potential corrosion inhibitors of zinc in acidic solution using weight loss measurements at 308K and 313K. MFGD is chosen based on the fact that it is commonly available throughout the year. It is also environmentally friendly and non-toxic. If it is found suitable, MFGD will add to the list of less expensive and eco-friendly corrosion inhibitors of plant origin. The study will also open up new research areas with regards to other metals and alloys using *Moraceae ficus glumosa delile* leaf extracts.

Experimental

Materials

The zinc sheets for this study were obtained from Jimeta-Yola in Adamawa State. The zinc sheets were mechanically press cut into 4.0 x 3.0 cm and thickness of 6.0×10^{-3} cm. They were degreased in absolute ethanol, dried in propanone and stored in moisture free desiccators before commencing corrosion studies. The average mass of the coupons was 7.92 – 8.00 g and total surface area of the coupons exposed was 16.4cm^2 [11].

Moraceae ficus glumosa delile leaves were obtained from Muva – village in Mubi – North Local Government Area of Adamawa State. The leaves were washed, dried at room temperature 25^{o}C (298 K). The leaves were pulverized and sieved. The fine particles of the leaves were extracted with ethanol and water respectively. The leaf powder, extracted in a conical flask after 24 hours, gave a better yield in ethanol than in water. A concentration range of 10.0, 30.0, 50.0, 70.0 and 100.0 mg/1000 mL of the extracts in 20 mL methanol – 80 mL water mixture was prepared and used as inhibitors at 308 K and 318 K. A concentration of 0.1 – 0.5 MH_2SO_4 (BDH grade) was prepared (using double distilled water) and used as blank (corrodent).

Mass loss Measurements

The procedure for mass loss determination was similar to that earlier reported by Onen [12] and Diksha Naik and Vashi [13]. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of mass loss is reported.

The effect of temperature on the corrosion rate of zinc coupon in 0.50 MH_2SO_4 at 318K was also studied with different concentrations (10 -100 mgdm^{-3}) of the extract. The reproducibility of the experiment was over 97 %.
Corrosion rates for zinc in 0.50M H_2SO_4 and different concentrations of MFGD were determined for 168 h immersion period from mass loss data using the formula

$$\text{Corrosion rate (mdd)} = \Delta m/\mathbf{dAT} \qquad (1)$$

Where, Δm is weight loss (g), d is the density of the metal, A is the area of zinc coupons and T is the time of exposure (hours) [12].

The percent inhibition efficiency (%I) was calculated using the expression

$$\%I = 1 - \frac{\rho_1}{\rho_0} \; x\, 100 \qquad (2)$$

Where, ρ_o and ρ_1 are the corrosion rates in uninhibited and inhibited in H_2SO_4 solutions respectively [12].

The surface coverage (θ) at each concentration of the inhibitor was determined using the relation

$$\theta = 1 - \frac{\rho_1}{\rho o} \qquad (3)$$

Where, ρ_o and ρ_1 are corrosion, rates, the absence and presence respectively of inhibitor in H_2SO_4 solutions at the same temperature [6].

Results and Discussion

Mass loss Measurements

The corrosion behaviour of zinc in H_2SO_4 with *Moraceae ficus glumosa delile* leaf extracts is given in **figure 1** and **Table 1**.

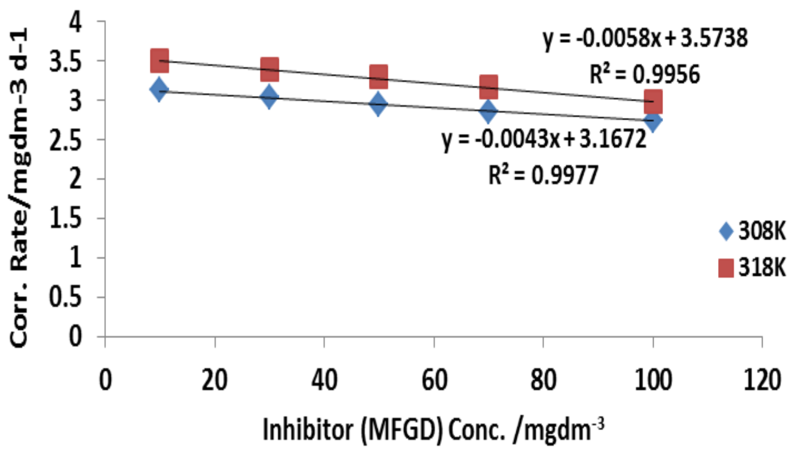

Figure 1 Variation of Corrosion Rate with Inhibitor (MFGD) Conc.in 0.50M H_2SO_4 at 308K and 318K.

It is observed from Table 1 and figure 1 that inhibition efficiency increases with additive (inhibitor) concentration but decreases with temperature while corrosion rate decreased with increase in additive (MFGD) concentration. This suggests that the inhibition process is due to the adsorption of MFGD on the zinc surface. The effectiveness of MFGD as a corrosion inhibitor of zinc in H_2SO_4 solution may be due to the presence of alkaloids, phenols and tannins. These phytochemicals contain –C=O, C=N, C=OH, Ph-OH e.t.c functional groups on their structures [14]. These groups adsorb on the zinc surface through their lone pairs of electrons. The lone pairs of electrons are delocalized and thus, produce resonance stabilization energies which stabilize the compounds. This assertion conforms to the views reported earlier [11].

It is evident from Table 1 and figure 2 that the inhibition efficiency (%I_E) and surface coverage (Θ) increased with inhibitor concentration and decreased with increasing temperature. This implies physical adsorption (physisorption) mechanism for the inhibition process. The high surface coverage's observed of high inhibitor concentration is due to very strong interaction between the adsorbed species. The surface coverage data indicate that the adsorption of MFGD (inhibitor) at the zinc interface may be due to electrostatic force between the metallic surface atoms and the adsorbate. This observation agrees with assertion earlier made [11, 15 - 16]. The adsorption of these compounds on zinc surface reduces the surface area available for attack of the aggressive ions from the acidic solution.

To further establish the extent of adsorption of inhibitor molecules on zinc surface, Langmuir isotherm was plotted as log C/Θ against C (inhibitor concentration) at 308K and 318K (figure 3). Similarly, Frumkin's adsorption isotherm was plotted as log C against the surface coverage (Θ) values at 308 and 318K (figure 4). The data obtained from this study between 308K and 318K, were found to fit Langmuir and Frumkin's adsorption models. This is an indication that corrosion inhibition of zinc is due to the formation and maintenance of a protective thin layer on metal surface. This affirms the assertion made by Ebenso *et al* [17] and enunciated in previous study by Onen and Kiri [18].

Table 1 Corrosion parameters for Zinc in 0.50M H_2SO_4 containing MFGD Leaf extract and blank from Mass loss Measurements at 308K and 318K

Inhibitor Conc.($mgdm^{-3}$)	Inhibtion efficiency (%I) 308K	318K	Corrosion rate (mdd) x 10^{-5} 308K	318K	Surface coverage (Θ) 308K	318K
Blank	-	-	7.89	7.97	-	-
MFGD						
10.0	60.37±0.91	56.04±1.21	3.13	3.51	0.60	0.56
30.0	61.48±1.05	57.51±0.87	3.04	3.39	0.62	0.58
50.0	62.59±0.78	58.61±0.96	2.95	3.30	0.63	0.59
70.0	63.70±1.22	60.07±0.11	2.86	3.18	0.64	0.60
100.0	65.19±2.15	62.64±1.02	2.75	2.98	0.65	0.63

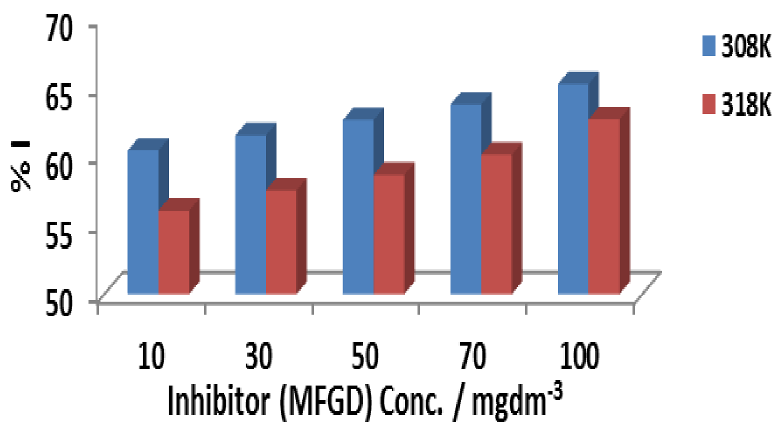

Figure 2 Variation of %I with Inhibitor (MFGD) Conc.in 0.50M H_2SO_4 at 308K and 318K.

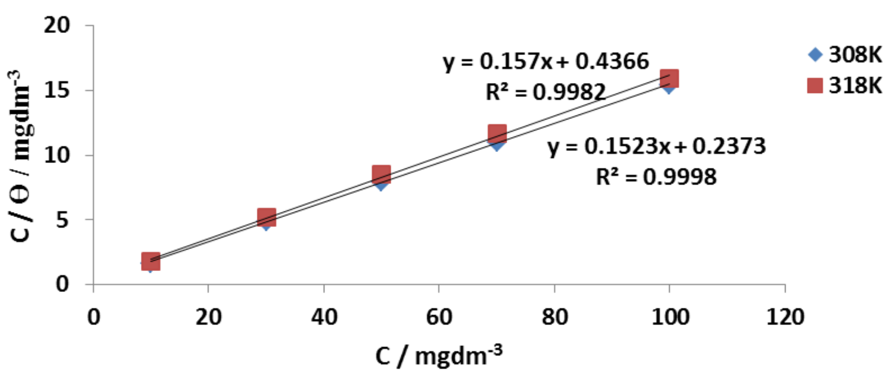

Figure 3 Langmuir Model for Zinc in 0.50M H_2SO_4 containing MFGD leaf-Extract at 308K and 318K for 168 hr

Kinetic and Thermodynamic Treatment of the Results

The rate constant, k, half life, $t_{1/2}$, activation energy of adsorption, Ea, standard heat of adsorption, Q°_{ads}, standard free energy change of adsorption, ΔG°_{ads} , standard enthalpy change of adsorption, ΔH°_{ads} and standard entropy change of adsorption, ΔS°_{ads} recorded in Tables 2 abd 3 are kinetic and thermodynamic parameters used in explaining the dynamics of the inhibition process. The k values were obtained from plots of log m_L against time while the rest of the parameters were determined using the following equations (4, 5, 6, 7, 8 and 9) respectively.

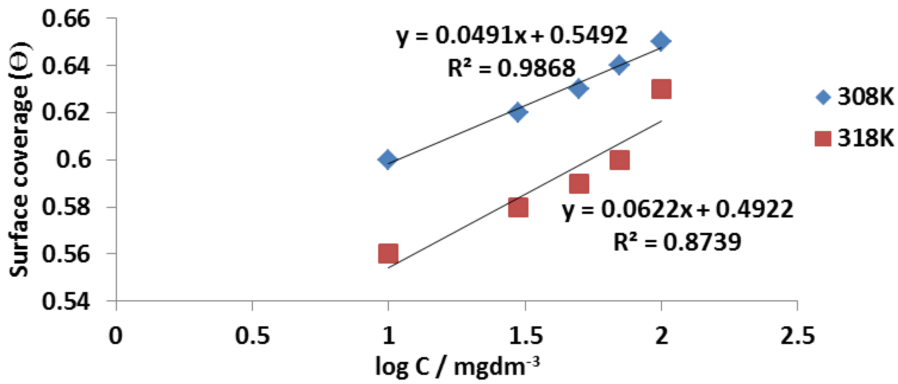

Figure 4 Frumkin adsorption isotherm plot for Zinc in 0.50M H_2SO_4 containing MFGD at 308K and 318K for 168 hr

$$t_{1/2} = 0.693/k \qquad (4)$$

$$Ea = \left[2.303\, R \frac{T_1 T_2}{T_2 - T_1}\right] log \frac{\rho_2}{\rho_1} \qquad (5)$$

$$Q^{\circ}_{ads} = \left[\log \frac{\theta_2}{1-\theta_1} - \log \frac{\theta_1}{1-\theta_1}\right]\left[\frac{T_1 T_2}{T_2 - T_1}\right] 19.147 \qquad (6)$$

Where, p_1, p_2, Θ_1 and Θ_2 are corrosion rates and surface coverages atT_1 (308K) and T_2 (318K) respectively [18].

$$\log C = \log (/1- \Theta) - \log B \quad (7)$$

where, log B = -1.74 – (ΔG°_{ads} /2.303RT) and C is the inhibitor concentration [13]. The values of B which show the binding power of the MFGD to the zinc surface can lead to the computation of the free energy change of adsorption, $\Delta G^{\circ}_{ads.}$

$$\Delta H^{\circ}_{ads} = Ea - RT \qquad (8)$$

$$\Delta S^{\circ}_{ads} = \Delta H^{\circ}_{ads} - \Delta G^{\circ}_{ads}/T \quad (9)$$

The values of k and $t_{1/2}$ in Table 2 indicate that the corrosion inhibition of zinc in H_2SO_4 containing MFGD follows first order reaction. More so, the mean value of Ea (8.50kJmol^{-1}) suggests physical adsorption of the inhibitor on the zinc surface. Inspection of Table 3 reveals that all the values of ΔQ°_{ads} and ΔG°_{ads} are negative. This implies that the inhibitor is strongly adsorbed on the zinc surface. The observation means that the adsorption process is exothermic and spontaneous. This affirms earlier reports by [6, 13, 18]. The negative values of ΔQ°_{ads} and ΔG°_{ads} further indicate strong interaction of the inhibitor on the zinc surface.

The values of ΔQ°_{ads} and ΔG°_{ads} are below -20.0 kJmol^{-1} which are consistent with the electrostatic interaction between the charged molecules and the charged metal surface(confirming physical adsorption). Values of ΔQ°_{ads} and ΔG°_{ads} more negative than -40 kJmol^{-1} involve charge transfer from the MFGD molecules to the zinc surface to form a coordinate bond (ie chemisorption). This agrees with the views expressed by Khaled [19].

The mean values of standard enthalpy change of adsorption, ΔH°_{ads} (5.94 kJmol^{-1}) and entropy change of adsorption, ΔS°_{ads} (5.95 kJmol^{-1}) respectively, are positive except for the blank. This shows that the desorption process is endothermic. The positive values of ΔH°_{ads} and ΔS°_{ads} signify that inhibition of zinc corrosion by MFGD is enhanced at low temperatures by absorbing heat. The negative values of ΔH°_{ads} and ΔS°_{ads} for the blank may be due to the fact that some amount of energy is released when H_2SO_4 reacts with zinc metal to liberate hydrogen gas as represented equation (10) below.

$$Zn\ (s) + H_2SO_{4\ (aq)} \rightarrow ZnSO_4\ (aq) + H_{2\ (g)}\ ;\ \ \Delta H^{\circ}_{ads} = -1.74\ kJmol^{-1} \quad (10)$$

Table 2 Kinetic parameters for Zinc in 0.50M H_2SO_4 containing MFGD Leaf extract and blank from Mass loss Measurements at 308K and 318K

System/Inhibitor Conc. (mg/dm^{-3})	Mean Mass loss (mg)		Rate constant, k (sec^{-1}) x 10^{-2}		Half- life, $t_{1/2}$ (sec) x10^2		Ea ($kJmol^{-1}$)
	308K	318K	308K	318K	308K	318K	
Blank	0.270	0.273	0.50	0.55	1.39	1.26	0.82
MFGD							
10.0	0.107	0.120	2.20	1.47	0.32	0.47	9.33
30.0	0.104	0.116	2.15	1.52	0.32	0.46	8.88
50.0	0.101	0.113	2.13	1.57	0.33	0.44	9.13
70.0	0.098	0.109	2.15	1.55	0.32	0.45	8.64
100.0	0.094	0.102	2.05	1.78	0.34	0.39	6.54
Mean							8.50

Table 3 Thermodynamic data for Zinc in 0.50M H_2SO_4 containing MFGD Leaf extract and blank from Mass loss Measurements at 308K

System/Inhibitor Conc. (mg/dm^{-3})	Q°_{ads} ($kJmol^{-1}$)	ΔG°_{ads} ($kJmol^{-1}$)	ΔH°_{ads} ($kJmol^{-1}$)	ΔS°_{ads} (kJK^{-1})
Blank	-	-	- 1.74	-1.74
MFGD				
10.0	-13.38	-5.40	6.77	6.79
30.0	-13.58	-2.80	6.32	6.33
50.0	-13.70	-1.61	6.57	6.58
70.0	-13.84	-0.85	6.08	6.08
100.0	-7.07	-0.05	3.98	3.98
Mean	-12.31	-2.14	5.94	5.95

MFGD inhibitor contains organic compounds with at least one polar unit having atoms of nitrogen, sulphur and oxygen. These polar organic compounds acting as corrosion inhibitors are adsorbed on the zinc surface, forming charge transfer complexes between their polar atoms and the metal surface. A similar assertion has been made by variuos workers [20]. *Moraceae ficus glumosa delile* decreases corrosion of zinc in H_2SO_4 through the reduction of reactivity of zinc.

Conclusion

The extract of MFGD inhibits the corrosion of zinc in 0.5M H_2SO_4 solutions, with inhibition efficiency of 65.19±2.15% at100 mg extract concentration and the inhibition efficiency decreased with increase in temperature. The adsorption of the inhibitor molecules was consistent with Langmuir and Frumkin's models and a first order kinetics was obtained from the kinetics consideration of the mass loss measurements.

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