Green Approach to Corrosion Inhibition of Mild Steel using Emilia Sonchifolia and Vitex Doniana in 2.5M HCl Medium

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Abstract:This research studied the use of leaves extract of Emilia sonchifolia and Vitex doniana as corrosion inhibitors of mild steel in 2.5M HCl medium using gasometric method at 30°C and 60°C. The result obtained showed that inhibition efficiency of Emilia sonchifolia leaves extract on the surface of the mild steel was 60.38% at 30°C and 53.13% at 60°C while that of Vitex doniana leave extract was 68.22% at 30°C and 54.98% at 60°C. Adsorption of Emilia sonchifolia leaves extract on the surface of the mild steel follows Langmuir, Tempkin and Freunlich adsorption isotherm while adsorption of Vitex donania leaves extract on the surface of the mild steel obeyed Langmuir and Tempkin adsorption isotherm. Physical adsorption was proposed from the Ea, ΔH and ΔG calculated.

Key words; corrosion, inhibitor, mild steel, Emilia sonchifolia and Vitex doniana

I. INTRODUCTION

Corrosion is the disintegration of an engineering material into its constituent atom due to chemical reaction with its surroundings or electrochemical oxidation of metal in reaction with an oxidant such as oxygen [1]. Typically, this type of damage produces oxide or salts of the original metal. Corrosion is a costly problem that results to economic waste when referring to cost of design, manufacturing, construction and management. This bitter aspect of corrosion is experienced mostly by the industries that are making use of mild steel especially chemical and allied industries. Mitigation of this problem of corrosion lies on the use of corrosion inhibitors, which help to prolong the life spasm of these materials. The use of synthetic inhibitors like chromium, cadmium, and lead based compound are considered as environmentally unsafe, because these elements are heavy metals [2]. Therefore, research is now geared towards using plant extract as corrosion inhibitors because they are non toxic, environmental friendly, easily biodegradable and renewable.

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The list of works done on the use of plants extract as corrosion inhibitors are endless, to mention but few are extract of fengrech seed and leave [3], L.Dopa [4], Azardiracta indica [5],Citrus aurantifolia [6] Pterocrpus soyauxi [7], Emblica officinalis (Indian Gooseberry) [8], Ricinus communis [9], Nypa friuticans wurmb [10], Tecoma stans [11], Blackpapper [12], Capparius decidua [13], Nyctanthes arbortisis [14] and Kalmegh (andrographis paniculata)[15].

The aim of this research is to compare the inhibitory action of *Emilia sonchifolia* (ES) and *Vitex doniana* (VD) on the surface of the mild steel using gasometric method at 30°C and at 60°C.

II. MATERIAL AND METHOD

A. *Preparation of Emilia sonchifolia and Vitex doniana leaves extract:*

1500g of *Emilia sonchifolia* leaves (ES) and 1500g of *Vitex doniana* leaves (VD) was air dried in a shade for 8-12 days and ground into powder. 350g of the powder was taken in 1000ml round bottom flask and enough quantity of ethanol was added as a solvent for extraction. The round bottom flask was covered with a stopper and left for 48hrs. Then the resulting paste was refluxed for 5hrs and filtered. The solvent was removed by concentrating the filtrate to about 20%. From this 0.1-0.5g/l concentration was made.

B. *Specimen preparation:*

Mild steel of thickness 1.4mm was obtained locally and was mechanically cut into coupons of 3×2×0.14cm. A small hole was drilled at one end of the coupons for easy hooking. The coupons were degreased in absolute ethanol, dried in acetone and stored in a desiccator.

C. *Test solution preparation:*

All the chemicals used were of Analytical grade. Solution was prepared by using double distilled water, and different concentrations of 1.0M – 2.5M HCl were prepared.

III. GASOMETRIC METHOD

Mild steel of 2 x 3 x 0.144cm was used here and this experiment was carried out at 30°C and 60°C.The procedure for this experiment has been documented in literature [16]-18]. From the volume of hydrogen evolved per minute, inhibition efficiency (I %) and degree of surface coverage (θ) were calculated using equation 1 & 2

$$I(\%) = \left(1 - \frac{V^1Ht}{V^0Ht}\right) \times 100 \quad (1)$$

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$$\theta = 1 - \frac{V^1 Ht}{V^0 Ht} \quad (2)$$

Where V^1_{Ht} and V^0_{Ht} are the volume of H_2 gas evolved at time t for inhibited and uninhibited solution respectively. Rate of hydrogen evolution was computed using equation 3 [19]

$$H_R = \frac{V_t - V_i}{T_t - T_t} \quad (3)$$

Where H_R is the rate of hydrogen evolution, V_t and V_i are the volume of hydrogen evolved at time T_t and T_i respectively.

IV. RESULTS AND DISCUSSION

Table 1 shows different concentrations of the ES and VD extract and inhibition efficiency. It could be deduced from the table that inhibition efficiency increase as the concentrations of the both extract increase with decrease in temperature inferring physical adsorption of the ES and VD extract on the surface of the mild steel.

V. ADSORPTION CONSIDERATION

The adsorption behavior of ES and VD extract was also studied. The test revealed that adsorption of ES extract on the surface of the mild steel is consistent with the Langmuir, Tempkin and Freundlich adsorption Isotherms. While the adsorption of VD extract on the surface of the mild steel obeyed Langmuir and Tempkin adsorption isotherms. Langmuir adsorption models can be represented as follows equation 6 [20]

$$\frac{C}{\theta} = C + \frac{1}{k} \quad (4)$$

Taking the logarithm of equation 4, equation 5 is obtained

$\log C/\theta = \log C - \log K$ (5)

Where C is the concentration of the inhibitor in the electrolyte, θ is the degree of surface coverage of the inhibitor and k is the equilibrium constant of adsorption. The plot of C/ θ versus C (fig 1and 2) gave linear plots indicating that Langmuir adsorption isotherm is applicable to the adsorption of ethanol extract of ES and VD on the surface of the mild steel.

Tempkin isotherm was also found to occur according to this equation 6 [21]–[22]

$$Exp(-2a\theta) = k \quad (6)$$

Where "a" is the Tempkin interaction parameter, θ is the degree of surface coverage of the inhibitor. K is the equilibrium constant of adsorption and C is the concentration of the inhibitor in the bulk electrolyte. Rearranging and taking logarithm of equation 6, equation 7 is obtained.

$$\theta = \frac{-2.303 logK}{2a} - \frac{2.303 logC}{2a} \quad (7)$$

$$Slope = -\frac{2.303}{2a}, \ Intercept = -\frac{2.303 logk}{2a}$$

Fig.3 and 4: Shows plot of θ versus log C. which was made from equation 6 and a linear graph was obtained which confirmed Tempkin adsorption isotherm for the adsorption of ES and VD extract on the surface of mild steel. Fig.5 revealed Freundlich's adsorption isotherm of the extract of ES on the surface of the mild steel and is given by the equation 8 and 9 [23]

$$\frac{x}{m} = KC^{1/n} \quad (8)$$

$$\log\frac{x}{m} = logK + \frac{1}{n}\log C \quad (9)$$

The fraction $\frac{x}{m}$ in equation 9 has been found to be approximate to the inhibition efficiency of the inhibitor, k and n is constant. Slope is equal to $\frac{1}{n}$ and intercept =l og k. Therefore, from equation 9, a plot of log inhibition efficiency (I %) versus log c produces a straight line that obeyed Freundlich adsorption isotherm [24], [25].

Table 1: Shows the concentration of the ES and VD extract and inhibition efficiencies at 30°C and 60°C from gasometric method.

Concentration of the inhibitors in(g/l)	Inhibition efficiency (%) from VD extract at 30°C	60°C	Inhibition efficiency (%) from ES extract at 30°C	60°C
0.1	23.51	21.11	28.18	22.00
0.2	38.35	30.20	40.25	33.78
0.3	45.13	38.39	49.78	37.97
0.4	51.06	42.29	57.20	46.48
0.5	68.22	54.98	60.38	50.13

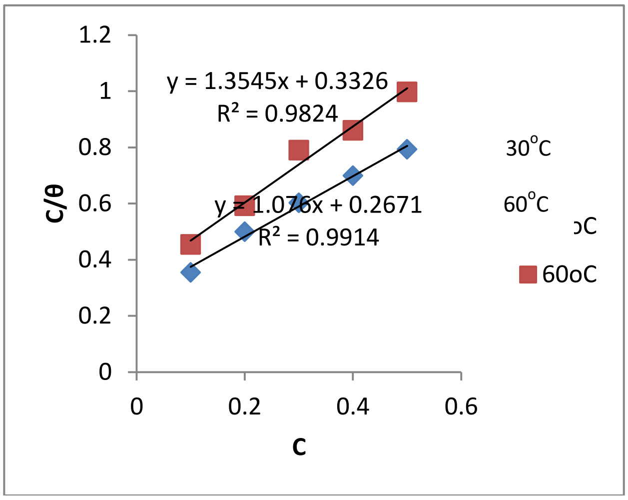

Fig. 1: Langmuir isotherm for the adsorption of ES extract on the surface of mild steel.

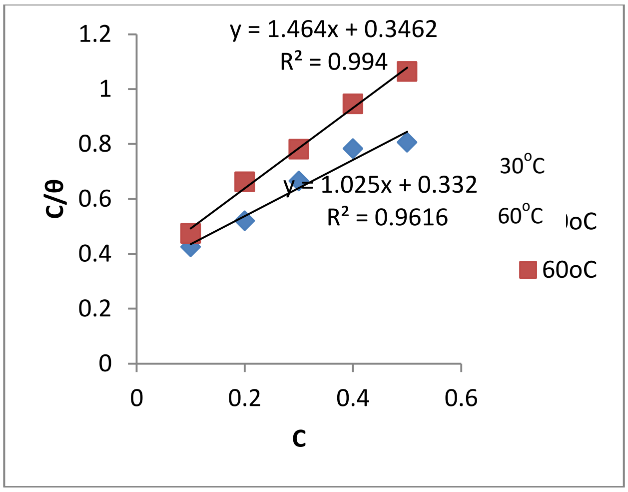

Fig. 2: Langmuir isotherm for the adsorption of VD extract on the surface of mild steel.

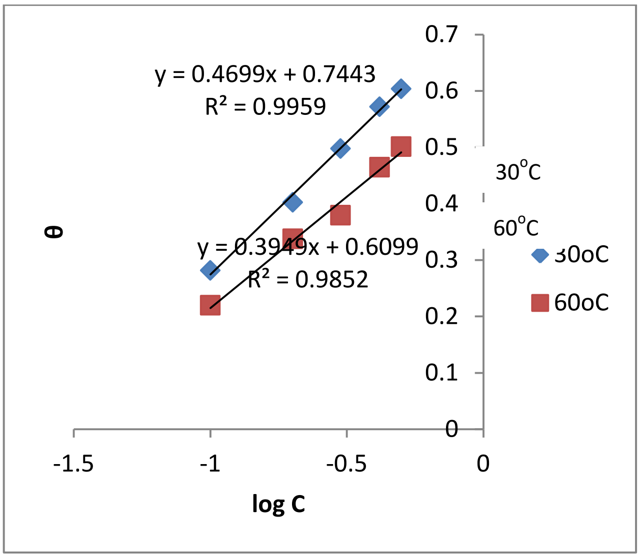

Fig.3: Tempkin isotherm for the adsorption of the of ES extract on the surface of the mild steel.

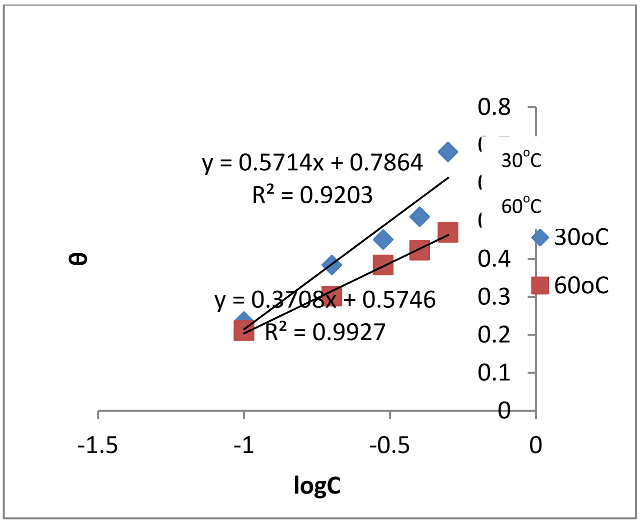

Fig.4: Tempkin isotherm for the adsorption of the leave extract of VD on the surface of the mild steel

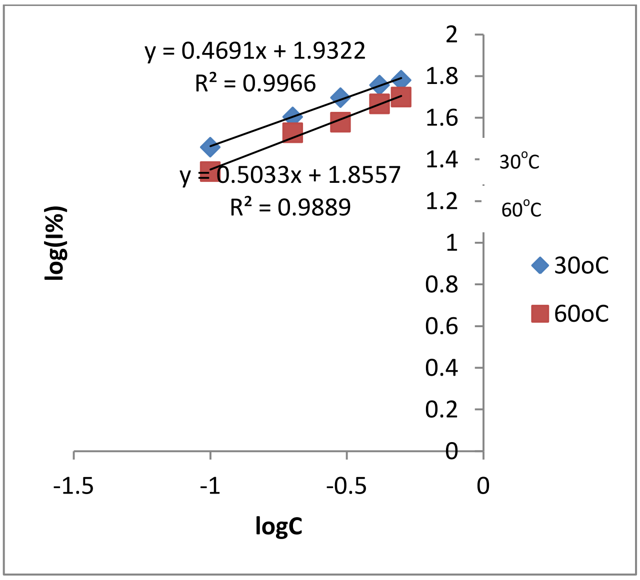

Fig.5: Freundlich isotherm for the adsorption of ES extract on the surface of the mild steel.

VI. THERMODYNAMICS STUDIES

The value of activation energy Ea was calculated using Arrhenius equation.

$$log \frac{H_{R2}}{H_{R1}} \frac{Ea}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right) \quad (10)$$

Where H_{R1} and H_{R2} are the hydrogen evolution rate at temperature T_1 and T_2 respectively. Table 2 shows the calculated values of Ea for ES and VD extract on the surface of the mild steel. It could be noticed that none of Ea reach up to the threshold value of 80KJmol^{-1} required for chemical adsorption, therefore, the adsorption is by physical adsorption mechanism [26]. Heat of adsorption is approximately equal to enthalpy of reaction ΔH_{ads}. The values of heat of adsorption were calculated using equation (11) [27]-[29].

$$\Delta H_{ads} = 2.303R\left[log\left(\frac{\theta 2}{1-\theta 2}\right) - log\left(\frac{\theta 1}{1-\theta 2}\right)\right] \times \frac{T1 \times T2}{T2 - T1} \quad (11)$$

Where θ_1 and θ_2 are degrees of surface coverage at temperatures, T_1 and T_2 respectively. Table 2: enumerated the values ΔH_{ads} at different concentrations of inhibitors. ΔH_{ads} were found to be negative in all the concentrations of the ES and VD extract showing that the reactions are exothermic. Values of adsorption parameter deduced from Langumir, Tempkin and Freundlich isotherms are recorded in Table 3 and 4. From the Tables the degrees of linearity (R^2) were also close to unity indicating strong adherence of the adsorption of ES and VD extract on the surface of the mild steel. The equilibrium constant of adsorption of ES and VD extract on the surface of the mild steel are related to the free energy of adsorption (ΔG_{ads}) according to equation 11

$$\Delta G_{ads} = -2.303RTlog(55.5)K \quad (11)$$

Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption, 55.5 is the molar heat of adsorption of water. Values of K obtained from intercept of Langumir, Tempkin and Freundlich isotherm were used to compute for ΔG_{ads} according to equation 11 and the result in Table 3 and 4.

From the result ΔG_{ads} values were found to be negative and less than the threshold value of -40KJmol^{-1} required for chemical adsorption hence the adsorption of ethanol extract of VD and PS on the surface of mild steel is spontaneous and follows physical adsorption mechanism [30]-[32].

Table 2: Calculated values of Ea and ΔH for ES and VD extract at different concentrations.

Concentration of VD and PS inhibitor in g/l.	Ea from ES inhibitor in KJ/mol	Ea from VD inhibitor in KJ/mol	ΔH from ES inhibitor in KJ/mol	ΔH from VD inhibitor in KJ/mol
0.1	58.37	31.18	-9.14	-3.88
0.2	62.95	41.24	-7.53	-10.39
0.3	53.38	36.38	-13.48	-7.72
0.4	48.46	38.30	-12.05	-9.91
0.5	44.26	37.42	-11.64	-17.05

Table 3: Langmuir, Tempkin and Freundlich adsorption isotherm parameters for adsorption of ES extract on the surface of the mild steel.

Temperature (^oC)	K_{ads}	Slope	ΔG ($kJmol^{-1}$)	R^2
	Langmuir			
30	3.7439	1.0760	-6.7635	0.9914
60	3.0069	1.3545	-8.0733	0.9824
	Tempkin	a		
30	35.0106	-2.4531	-9.3756	0.9959
60	38.4769	-2.9154	-9.7524	0.9852
	Freundlich			
30	85.5067	0.4691	-11.7792	0.9966
60	71.7533	0.5033	-12.8836	0.9889

Table 4: Langmuir and Tempkin adsorption isotherm parameters for adsorption of ethanol extract of VD.

Temperature (^oC)	k_{ads}	Slope	ΔG (KJ/mol)	R^2
	Langmuir			
30	3.0095	1.0250	-7.3444	0.9616
60	2.8880	1.4640	-8.1840	0.9940
	Tempkin	a		
30	23.7903	-2.0151	-9.5141	0.9203
60	34.7536	-3.1050	-9.5870	0.9927

VII. CONCLUSION

ES and VD extract showed inhibitive effect on corrosion of mild steel in acidic environment. Inhibition efficiency increase with an increase in inhibitor concentration for both extracts. The adsorptions of ES extract on the surface of the mild steel followed Langmuir, Tempkin and Freundlich while that of VD extract obeyed langmuir and Tempkin adsorption isotherms. ES extract proved to be better corrosion inhibitor than VD extract since it has higher inhibition efficiency. Finally, the mechanism of physical adsorption was proposed from the calculated values of Ea, ΔH_{ads}, and $\Delta G_{ads,}$ obtained.

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