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Corrosion Inhibition and Adsorption Studies of Ethanol Extract of *Senna alata* for Mild Steel in 2.0M H_2SO_4 Solution

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Abstract

Senna alata leaves extract was used as corrosion inhibitor of mild steel in 2.0M H_2SO_4 solution at 30°C and at 60°C using weight loss method. The result obtained showed that at 30°C the inhibition efficiency was 71.86% and 66.52% at 60°C. The corrosion rate of mild steel increases from 0.5M to 2.0M of H_2SO_4 and decreases from 0.1g/l to 0.5g/l of the ethanol extract of *Senna alata*. The calculated ΔE, ΔG, and ΔH indicated that the adsorption of ethanol extract of *Senna alata* was by Physical adsorption. Also adsorption of *Senna alata* leaves extract on the surface of the mild steel follows Langmuir, and Freundlich adsorption isotherms.

Keywords

Corrosion, Inhibition, Mild Steel, *Senna alata*

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1. Introduction

Corrosion control measures using natural product extract has draw a lot of attention these days because it is environmentally friendly, cheap, biodegradable and renewable. Corrosion is unwanted oxidation of a metal [1]. It is an ugly menace that ends up destroying any metal it attacks. The mechanism of corrosion is a Redox reaction where there is transfer of electron from one atom to another. It is triggered by the presence of moisture, aqueous electrolytes, and gases like O_2, SO_2, CO_2, impurities, and reactivity of a metal. Corrosion occurs at the anode, for example when metallic iron is exposed to moist air, Iron is oxidized to Fe^{2+} which passes into the solution in the water drop. The electrons released by the Fe oxidation are used to reduce oxygen at the cathode. The electrochemical reactions are;

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Anode: $2Fe \rightarrow 2Fe^{2+} + 4e^-$ The overall reaction is;

Reaction 1: $O_2 + 4H^+ + 2Fe \rightarrow 2H_2O + 2Fe^{2+}$

The Fe^{2+} ions in solution are further oxidized to Fe^{3+} by oxygen, either in solution or at the surface. The Fe^{3+} precipitates as Fe_2O_3 or rust. Oxygen from the atmosphere is again the oxidizing agent. The electrochemical reactions are;

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Anode: $4Fe^{2+} \rightarrow 4Fe^{3+} + 4e^-$ Therefore, the overall reaction here is;

Reaction 11: $O_2 + 4H^+ + 4Fe^{2+} \rightarrow 4Fe^{3+} + 2H_2O$

The overall reaction for the corrosion of Iron can be obtained by combining reaction 1 and 11, multiply reaction 1 by 2 in order to deliver the four Fe^{2+} ion required in reaction 11. The Fe^{2+}ions then cancel in the summation.

Reaction 1: $2O_2 + 8H^+ + 4Fe \rightarrow 4H_2O + 4Fe^{2+}$

Reaction 11: $O_2 + 4H^+ + 4Fe^{2+} \rightarrow 4Fe^{3+} + 2H_2O$

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$3O_2 + 12H^+ + 4Fe \rightarrow 4Fe^{3+} + 6H_2O$

The six H_2O molecules can be viewed as $12H^+$ and $6O^{2-}$ in which case, the $12H^+$ on each side conceal finally, $4Fe^{3+}$ + $6O^{2-}$ is equivalent to $2Fe_2O_3$, which allows us to write the common representation of the overall process of corrosion of iron as $3O_2 + 4Fe \rightarrow 2Fe_2O_3$ [1]. There are four types of Corrosion control measures; Cathodic protection, Coating and Passivators, and inhibitors. But corrosion inhibitors have gained more popularity because of it cheapness, renewability and environmentally friendliness. These inhibitors are mainly organic products or natural products. Inhibitors acts by adsorbing on the surface of the reacting metal, thereby blocking the active sites of corrosion and restrict the rate of anodic or cathodic process or it may increase the electrode potential. Corrosion inhibition using plants extract has been studied by a lot of researchers, to mention but few in the long list include the following; *Cucurbitamaxima* [2], *Morinda tinctoria*[3], *Eupatorium Odoratus* [4], *Musa acuminata* [5], *Piper Nigrum L.* [6], *Xylopia ferrugiular* [7], *Citrus aurantifolia* [8], Curry leaf [9], *Pterocarpus soyauxi* [10], *Emilia sonchifolia* [11], *Vitex doniana* [12], *Chlomolaena odorata* [13] *Cocos nucifera* [14], *Jatropha curcas* [15]. The aim of this work is to investigate the action of *Senna alata* leave extract as corrosion inhibitor of mild steel in 2.0M tetraoxosulphate (vi) acid, (H_2SO_4) solution using Gravimetric techniques.

2. Experimental Method

2.1. Preparation of *Senna alata* Leaves Extract

Leaves of *Senna alata (*SA) was air dried in a shade for 21 days and ground into powder. 450g 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. It was filtered after 48hrs. Solvent was removed from the filtrate by concentrating the filtrate to about 10%. From this 0.1-0.5g/l concentration of the extract was made.

2.2. Specimen Preparation

Mild steel of thickness 1.4mm was obtained locally and was mechanically cut into rectangular shape of 4×4×0.14cm. A small hole was drilled at one end of the rectangular mild steel for easy hooking. The rectangular mild steels were degreased in absolute ethanol, dried in acetone and stored in a desiccator.

2.3. Test Solution Preparation

All the chemicals used were of Analytical grade. Solution was prepared by using double distilled water, and different concentrations of 0.5Mol/dm^3 – 2.0Mol/dm^3 of H_2SO_4 were prepared.

2.4. Gravimetric Method

This experiment was carried out at temperatures 30°C and 60°C. The weighed mild steels of 4 x 4 x 0.144cm were inserted into 250ml beakers containing 200ml of different acid concentrations, 0.5moldm^{-3}-2.0moldm^{-3} H_2SO_4 with the help of a thread and were put in a thermostated water bath. The mild steels were removed each day i.e. at 24hr interval for 5days (120hrs). The mild steels were washed several times in 10% Na0H solution with bristle brush, rinsed with distill water and dried in acetone and then re-weighted. This experiment was repeated with various concentrations of inhibitor in 2.0moldm^{-3} H_2SO_4. The differences in weight of the mild steels were taken as the weight loss which was used to compute the corrosion rate given by;

$$\text{Corrosion rate (mpy)} = \frac{543x}{rAt} \quad (1)$$

Where x is weight loss (g), r is the density of specimen (gcm^{-3}), A is surface area of the specimen (cm^2) and t is the exposure time (days). The inhibition efficiency of SA was calculated using the expression:

$$I\% = \left(\frac{X_O - X_1}{X_O}\right) \times 100 \quad (2)$$

Where X_0 and X_1 are the weight loss of mild steel in the absence and presence of inhibitor in H_2SO_4 medium at the same temperature. The degree of surface coverage (θ) was also calculated using the equation: [16]

$$\theta = \frac{X_O - X_1}{X_O} \quad (3)$$

3. Result and Discussion

3.1. Gravimetric Method

The result of the gravimetric method was explained with a plot of weight loss of the mild steel with various concentrations of the inhibitor in 2M H_2SO_4 at different temperatures ie 30°C and 60°C against time in fig. 1 and 2. It can be inferred from the graph that the weight loss of the mild steel decreases as the concentration of the inhibitor increases when compared with the blank experiment. It was also observed that as the time increases from day 1 to day 5, the ethanol extract of *Senna alata* inhibited corrosion of the mild steel through decrease in the measurement of weight loss obtained at various days. The result equally showed that weight loss of the mild steel increases with an increase in temperature from 30°C to 60°C when compared with the blank experiment.

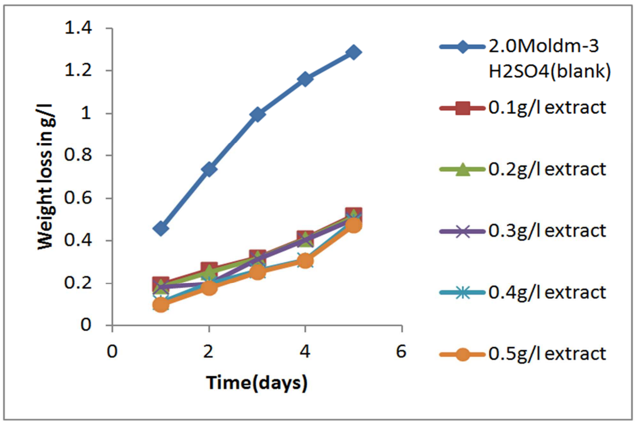

Fig. 1. Weight loss of mild steel against time in the various concentrations of ethanol extract of SA in 2M H_2SO_4 solution at 30°C.

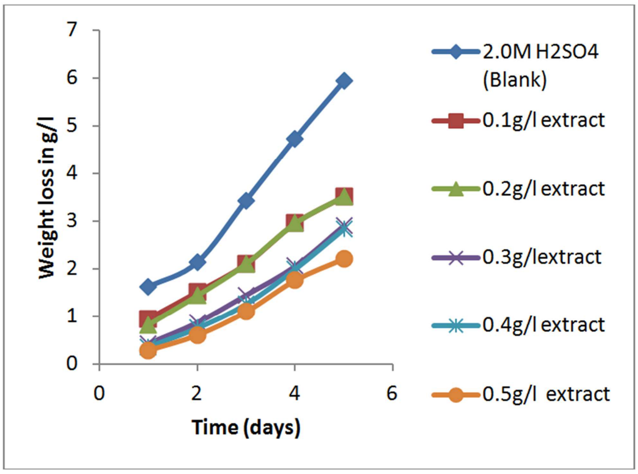

Fig. 2. Weight loss of mild steel against time in the various concentrations of ethanol extract of SA in 2M H_2SO_4 solution at 60°C.

3.2. Adsorption Study

The result in table 1 revealed that inhibition efficiencies and degree of surface coverages increase with an increase in SA concentrations and decrease with temperature. Increase in inhibitor efficiencies and degree of surface coverages with decrease in temperature suggested physical adsorption mechanism. The mechanism of the adsorption is that *Senna alata* leaves extract blocked the discharge of hydrogen ion, H^+ and dissolution of the metal ion. Also the acid pickling, SA extract has polar groups like organic N, S, and OH which can attach itself to the metal surface thereby preventing further attack of the corrosion [17]. Furthermore, this study was subjected to various adsorption isotherms with the data obtained from weight loss. Langmuir and Freundlich adsorption isotherms fitted most and the result in fig 3 and 4.

Fig. 3, revealed Freundlich's adsorption isotherm of SA extract on the surface of the mild steel and is given by the equation 5 and 6 [18]

$$\frac{x}{m} = kc^{1/n} \tag{4}$$

$$\text{Log}\,\frac{x}{m} = \log k + \frac{1}{n}\log c \tag{5}$$

The fraction $\frac{x}{m}$ in equation 5 has been found to be approximate to the inhibition efficiency of the inhibitor, k and n are constant. Slope is equal to $\frac{1}{n}$ and intercept = l og k. Therefore, from equation 5, a plot of log inhibition efficiency (I%) versus log c produces a straight line that obeyed Freundlich adsorption isotherm. [19].

Assumption of Langmuir adsorption isotherm can be expressed by equation 6 [20]

$$C/\theta = C + 1/k \tag{6}$$

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. Taking logarithm of both sides of equation 6, equation 7 is obtained.

$$\log C/\theta = \log C - \log k \tag{7}$$

The plot of log(C/θ) versus logC was made and the result obtained is as shown in fig.4, indicating that the adsorption of ethanol extract of SA obeyed Langmuir adsorption isotherm. Values of adsorption parameters deduced from Langmuir adsorption plot are shown in Table 3. The values of degree of linearity (R^2) were found to be close to unity indicating strong adherence of the adsorption of ethanol extract of SA to Freundlich and Langmuir adsorption isotherms.

Table 1. Shows the calculated inhibition efficiencies and degree of surface coverages for the inhibition of mild steel at different concentrations of SA in 2.0M H_2SO_4 medium.

Concentration of SA inhibitor in g/l	Inhibition efficiencies (%) at		Degree of surface coverages (θ) at	
	30°C	60°C	30°C	60°C
0.1	63.09	38.21	0.6309	0.3821
0.2	63.85	41.23	0.6385	0.4123
0.3	65.54	56.70	0.6554	0.5670
0.4	70.35	63.40	0.7035	0.6340
0.5	71.86	66.52	0.7186	0.6652

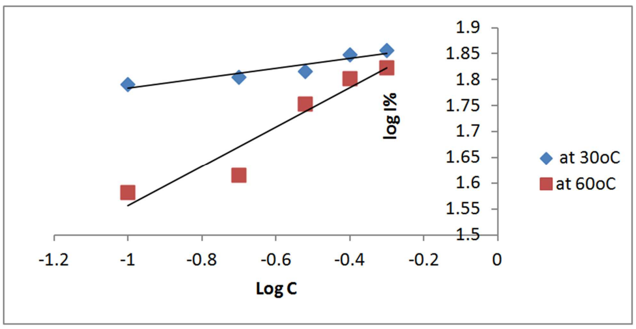

Fig. 3. Freundlich Isotherm for the adsorption of ethanol extract of SA on the surface of the mild steel.

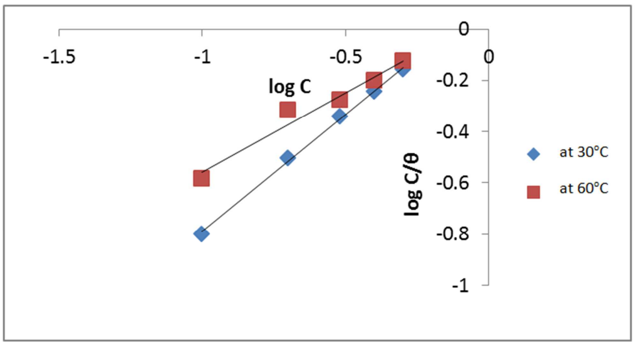

Fig. 4. Langmuir adsorption isotherm for the adsorption of the ethanol extract of *Senna alata* on the surface of the mild steel.

3.3. Thermodynamics Studies

The effect of temperature on the corrosion of mild steel at various concentration of SA was also calculated using Arrhenius equation 8

$$CR = A\exp(-Ea/RT) \quad (8)$$

Where CR is the corrosion rate of mild steel, A is the Arrhenius or pre-exponential constant, Ea is the activation energy, R is the gas constant and T is the temperature. Assuming that corrosion rate of mild steel at temperature of 30°C (T_1) and 60°C (T_2) are CR_1 and CR_2, then equation 8 can be transformed into logarithm function as expressed by equation 9

$$\log\frac{CR_2}{CR_1} = \frac{Ea}{2.303R} \times \frac{1}{T_1} - \frac{1}{T_2} \quad (9)$$

Values of activation energy are presented in table 2, the values were found to decrease from -52.14KJ/mol to -40.76kJ/mol with an increase in the concentration of ethanol extract of SA. This shows that ethanol extract of SA was physically adsorbed on the surface of the mild steel [21]. Table 2, also shows the result of the calculated heat of adsorption, ΔH_{ads} of ethanol extract of SA on the surface of mild steel using equation 10 [22]

$$\Delta H_{ads} = 2.303R\,[\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1)] \times (T_2T_1/T_2-T_1) \quad (10)$$

Where θ_1 and θ_2 are the degree of surface coverages at temperature T_1 and T_2 respectively. The values of ΔH_{ads} were negative and ranged from -33.50KJmol^{-1} to -7.019kJmol^{-1} indicating that the adsorption of ethanol extract of SA is exothermic [23].The equilibrium constant of adsorption of ethanol extract of SA is related to the free energy of adsorption (ΔG_{ads}) according to the following equation.

$$\Delta G_{ads} = -2.303RT\log(55.5k) \quad (11)$$

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 Langmuir and Freundlich isotherms were used to compute values of ΔG_{ads} according to equation 11 and the result in table 3. 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 *Senna alata* on the surface of mild steel is spontaneous and follows physical adsorption mechanism [24-25].

Table 2. Calculated values of Activation energy and Heat of adsorption at various concentration of the inhibitor.

Concentration of inhibitor in g/l	Ea(KJ/mol)	ΔH_{ads}(kJ/mol)
0.1	-52.14	-33.50
0.2	-51.32	-25.82
0.3	-44.11	-9.97
0.4	-43.66	-8.80
0.5	-40.76	-7.02

Table 3. Langmuir and Freundlich adsorption isotherm parameters for adsorption of ethanol extract of SA on the surface of the mild steel.

Temperature (°C)	Log k	Slope	ΔG (kJmol^{-1})	R^2
	Freundlich			
30	1.8787	0.0949	-11.71	0.8870
60	1.9370	0.3800	-12.95	0.9120
	Langmuir			
30	-0.1260	0.9166	-4.902	0.9630
60	-0.0622	0.6192	-3.432	0.9980

4. Conclusion

SA extract showed inhibitive effect on corrosion of mild steel in acidic environment. Inhibition efficiencies increase with an increase in inhibitor concentrations. The adsorption of SA extract on the surface of the mild steel followed Langmuir and Freundlich adsorption isotherms. The mechanism of physical adsorption was confirmed from the calculated values of Ea, ΔH_{ads}, and $\Delta G_{ads,}$ obtained.

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