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Research Article

CORROSION INHIBITION OF MILD STEEL BY *PTEROCARPUS SOYAUXI* LEAVES EXTRACT IN HCL MEDIUM.

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ABSTRACT: Corrosion inhibition of mild steel using *pterocarpus soyauxi,* (PS) was studied using weight loss measurement at 30ºC and 60ºC. The inhibition efficiency increased with an increase in inhibitor concentration but decreased with temperature. The inhibition of corrosion of mild steel obeyed Tempkin and Freundlich adsorption isotherms and fitted into First Order reaction kinetics. Some thermodynamics parameters, such as Ea, ΔH, and ΔG, were calculated and all indicated that inhibition of corrosion of mild steel by ethanol extract of PS was by Physical adsorption mechanism.

Keywords; corrosion, inhibition, mild steel, *Pterocarpus soyauxi extract*

INTRODUCTION

The use of corrosion inhibitors has become an answer to the corrosion attack of mild steel which always lead to damage and total replacement of these mild steels. Most studies on corrosion inhibitor reported that a large number of inhibitors are organic compound with N, S, and O hetro atoms, they have higher electron density, making them the reaction centres [1-5]. These compounds are adsorbed on the metallic surface and block the active corrosion sites; most of them are highly toxic to both human beings and the environment. Hence the use of Natural products as eco-friendly and harmless corrosion inhibitors has gained popularity [6-8]. This is because they can be extracted at low cost, easily available, biodegradable and poses no harm to the environment. Many plant extracts have been used as corrosion inhibitors such as aqueous extract of *kalmegh (Andrographis paniculata)*[9], *Capparius deciduaina* [10] black pepper extract [11] extrudate from *Pachylobus edulia* [12] gum extrudate from *Acacia seyal var* [13], *citrus aurantiifolia* [14], *Nyctanthes arbortistis [8], Bauhinia purpurea [15] and Emblica officinalis [16]*

Ptercarpus soyauxi, a *papilionodeae* family plant with a vernacular name Oha-ocha is an annual plant with a long history of traditional medicinal uses in Nigeria. It is a Monocotyledon and a broader nerves but not entirely constant. The phytochemical screening of the PS leaves showed the presence of saponins, flavanoids, Steroid, terpenoids, tannins, alkaloids, resin and glycoside [17]. The aim of work is to investigate the inhibitory action of the leaves extract of *Pterocarpus soyauxi* on the corrosion of mild steel in HCl medium using weight loss method. However, the leaves of PS have never been used as a corrosion inhibitor in acidic medium.

MATERIALS AND METHODS

Preparation of *Pterocarpus soyauxi* leaves extract:

1424g of leaves of *Ptercarpus soyauxi (*PS) 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.

Specimen preparation:

Mild steel of thickness 1.4mm was obtained locally and was mechanically cut into coupons of 4×4×0.14cm and 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.

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.

Gravimetric Method

This experiment was done at temperatures 30ºC and 60ºC. In this experiment, 250ml beakers were used. The weighed mild steel of 4 x 4 x 0.144cm was inserted into a beaker containing 200ml of different acid concentrations, 1.0M– 2.5M HCl with the help of a thread and was put in a thermo stated water bath. The coupons were removed each day i.e. at 24hr interval for 7days (168 hrs). The coupons were washed several times in 15% Na0H solution with bristle brush, rinsed with distill water and dried in acetone and then reweighted [2]. This experiment was repeated with various concentrations of inhibitor in 2.5M HCl. The differences in weight of the coupons were taken as the weight loss which was used to compute the corrosion rate given by;

$$\text{Corrosion rate (mpy)} = \frac{543w}{rAt} \qquad (1)$$

Where W 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 VD was calculated using the expression:

$$I\% = (W_0 - W_1 / W_0) \times 100 \qquad (2)$$

Where W_0 and W_1 are the weight loss of mild steel in the absence and presence of inhibitor in HCl medium at the same temperature. The degree of surface coverage (θ) was also calculated using the equation:

$$\Theta = (W_0 - W_1) / W_0 \qquad (3)$$

RESULTS AND DISCUSSION

Weight Loss Method

Fig.1 represents the corrosion rate against corrodent concentration for mild steel at temperature 30^0C and 60^0C. From the fig 1, it was found that corrosion rate increased as the concentration of the acid increased. This observation is due to the fact that the rate of chemical reaction increases as the concentration of active species, temperature and time increases.

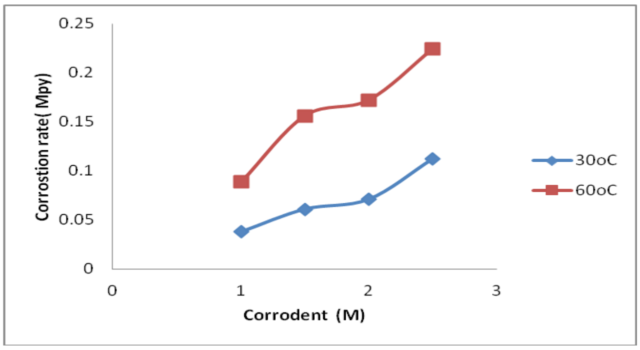

Fig.1: Plot of corrosion rate against corrodent concentration for mild steel corrosion at 30ºC and 60ºC

Effect of Inhibitor Concentration

Fig.2 shows the plot of corrosion rate against inhibitor concentration for the corrosion of mild steel in 2.5M HCl at 30^0C and 60^0C . The figure showed that the corrosion rate decreases as the concentration of the inhibitor increases at 30^0C and 60^0C. Fig.3 and 4 revealed the variation of weight loss with time in the absence of inhibitor at 30^0C and 60^0C and in the presence of different concentration of PS inhibitor at 30^0 and 60^oC. It was obtained from the plot that weight loss of mild steel decreases as the concentration of the PS extract increases compared to the blank experiment. This was because ethanol extract of PS had adsorbed on surface of mild steel thereby inhibiting corrosion.

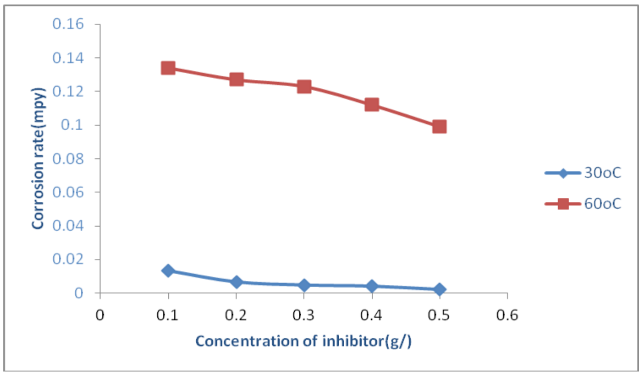

Fig 2: Plot of corrosion rate against concentration of ethanol extract *pterocarpus soyauxi* at 30°C and 60°C

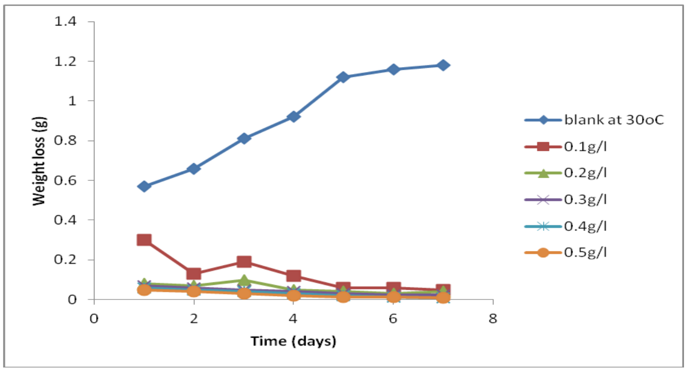

Fig.3: variation of weight loss against time in the presence and absence of ethanol extract of *Pterocarpus soyauxi* at 30°C

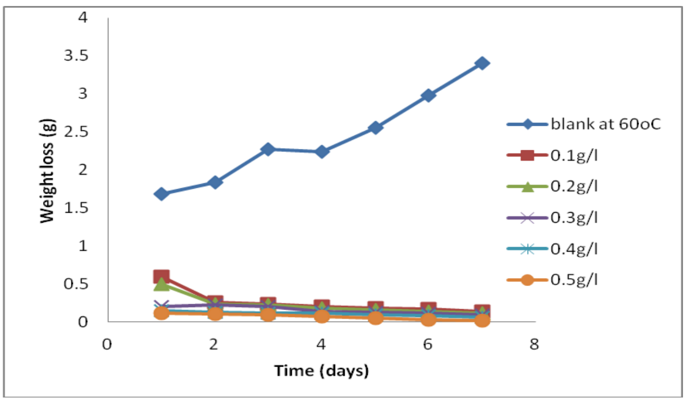

Fig. 4: Variation of weight loss with time in the presence of ethanol extract of *Pterocarpus soyauxi* at 60°C

Fig.5 is the plot of In (weight loss) against time, a linear graph was obtained showing that the reaction is first order. Table 1 shows that rate constant K_1 and half life $t_{1/2}$ are constant confirming this first order reaction.

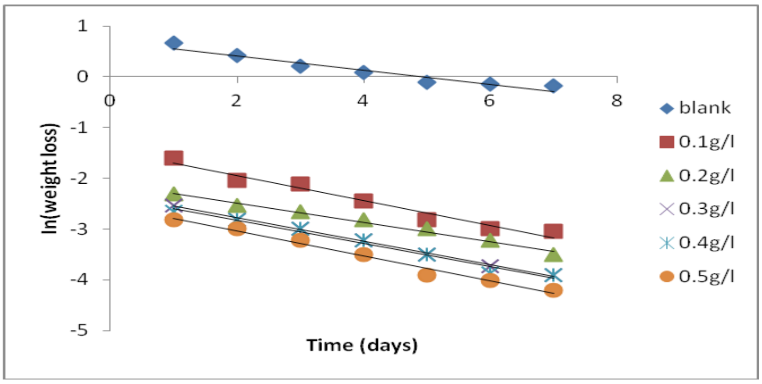

Fig.5: Kinetic plot for inhibition of the corrosion of mild steel by ethanol extract of *Pterocarpus soyauxi* at 30°C.

Table 1 : Rate constant (k_1) and half life ($t_{1/2}$) for the corrosion of mild steel in the presence of ethanol extract of *Pterocarpus soyauxi*

Concentration of Inhibitor in g/l	K_1	$t_{1/2}$
0.1	0.2	3.5
0.2	0.2	3.5
0.3	0.2	3.5
0.4	0.2	3.5
0.5	0.2	3.5

Adsorption Consideration:

Table 2, depicts that inhibition efficiency increases with increase in PS concentration and with decrease in temperature. Increase in inhibitor efficiency with decrease in temperature suggested physical adsorption mechanism. The character of adsorption of PS extract was further elucidated from degree of surface coverage (θ). Fig.6, Shows plot of θ versus log C, Tempkin adsorption of PS extract of mild steel corrosion at 30°C and 60°C Tempkin adsorption isotherm is known with this equation [18-20]

$$\theta = \frac{-2303\log K}{2a} - \frac{2303\log C}{2a} \quad (4)$$

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 PS inhibitor. For Freundlich's adsorption isotherm a plot of log[1%] against logC. Fig. 7, which is linear graph, was obtained, showing that the adsorption of ethanol extract of PS on the surface of the mild steel obeys Freundlich's adsorption isotherm [4, 21].

Table 2: calculated inhibition efficiency and degree of surface coverage for the inhibition of mild steel at different concentrations of PS in HCl medium.

Concentration of PS inhibitor in g/l	Inhibition efficiency (%) at		Degree of surface coverage (θ) at	
	60°C	30°C	60°C	30°C
0.1	88.19	50.47	0.8810	0.5047
0.2	93.98	53.10	0.9398	0.5310
0.3	94.15	54.68	0.9415	0.5468
0.4	94.94	58.80	0.9494	0.5880
0.5	96.48	63.55	0.9648	0.6355

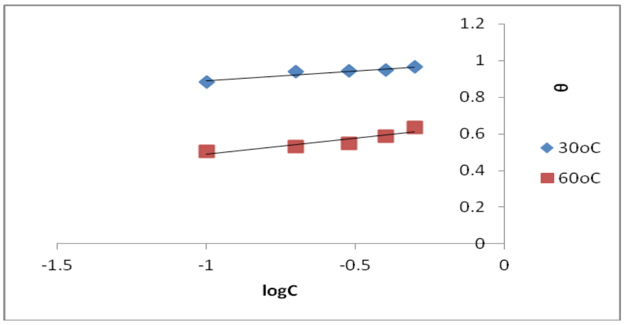

Fig.6: Tempkin isotherm for the adsorption of the ethanol extract of *pterocarpus soyauxi* on the surface of the mild steel.

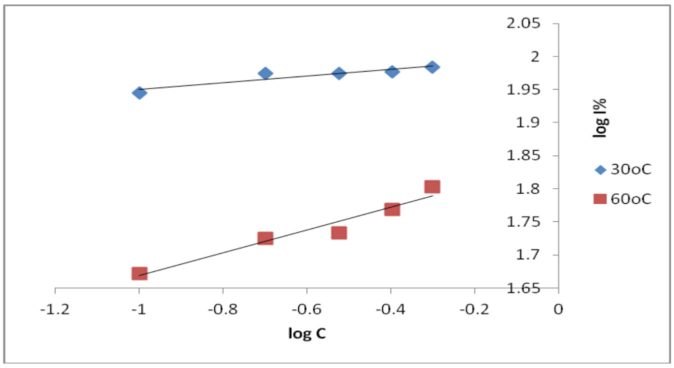

Fig.7: Freundlich isotherm for the adsorption of ethanol extract of PS on the surface of the mild steel.

Thermodynamics Studies

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

$$\text{Log}\frac{CR2}{CR1} = \frac{Ea}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right) \quad (5)$$

Where CR_1 and CR_2 are the corrosion rate at temperature T_1 and T_2 respectively. The values of Ea were found to decrease with increase in the concentration of PS. The values of heat of adsorption were calculated using equation (11) [22, 23]. Heat of adsorption is approximately equal to enthalpy of reaction ΔH_{ads}

$$\Delta H_{ads} = 2.303R\ [\log\left(\frac{\theta 2}{1-\theta 2}\right) - \log\left[\frac{\theta}{1-\theta 1}\right] \times \left[\frac{T1\ X\ T2}{T2 - T1}\right] \quad (6)$$

Where θ_1 and θ_2 are degree of surface coverage at temperatures, T_1 and T_2 respectively. Table 2: enumerated the values ΔEa and ΔH_{ads} at different concentrations of inhibitor, the values of Ea were found to increase with increase in the concentrations of PS inhibitor. This depicted that the PS was physically adsorbed on the surface of the mild steel preventing further corrosion attack due to the phytochemical constituents it contained. ΔH_{ads} were found to be negative in all the concentrations of the PS extract showing that the reaction is exothermic. Values of adsorption parameter deduced from Tempkin and Freundlich isotherms are recorded in Table 3: From the Tables the degrees of linearity (R^2) were also close to unity indicating strong adherence of the adsorption of ethanol extract of PS. The equilibrium constant of adsorption of ethanol extract of PS is related to the free energy of adsorption (ΔG_{ads}) according to equation 7

$$\Delta G_{ads} = -2.303RT\log(55.5K) \quad (7)$$

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 Tempkin and Freundlich isotherm were used to compute values of ΔG_{ads} according to equation 7 and the result in Table 4.

Table 3: some thermodynamics parameters for the adsorption of ethanol extract of *pterocarpus soyauxi* on the surface of mild steel.

Concentration of inhibitor in g/l	Ea(kJ/mol)	ΔH_{ads}(kJ/mol)
0.1	64.90	-55.60
0.2	82.38	-73.39
0.3	90.14	-72.47
0.4	91.55	-70.91
0.5	108.26	-77.06

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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 PS on the surface of mild steel is spontaneous and follows physical adsorption mechanism [24- 26].

Table 4: Tempkin and Freundlich adsorption isotherm parameters for adsorption of ethanol extract of *Pterocarpus soyauxi*

Temperature (°C)	Log K	Slope	ΔG_{ads} (KJ/Mol)	R^2
	Temkin	A		
30°C	0.9977	4.6729	-10.11	0.8895
60°C	0.6613	2.9223	-9.98	0.8429
	Freundlich			
30°C	2.0000	0.0509	-11.87	0.8714
60°C	1.8417	0.1733	-22.02	0.9429

Conclusion

PS extract showed inhibitive effect on corrosion of mild steel in acidic environment.
Inhibition efficiency increase with an increase in inhibitor concentration as a result of the phytochemical constituents of the PS extract.
The adsorption of PS extract obeyed Langmuir and Tempkin adsorption isotherms.
Physical adsorption was proposed from the calculated values of Ea, ΔHads, and ΔGads, obtained. Also the inhibition efficiency of PS decreases as the temperature increases, which depicts that adsorption process of PS, is physical in nature.

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