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INHIBITION OF CORROSION OF MILD STEEL IN ALKALINE MEDIUM BY ETHANOL EXTRACT OF *PTEROCARPUS SOYAUXII* Taub LEAVES

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ABSTRACT

The inhibition of corrosion of mild steel by ethanol extract of *Pterocarpus soyauxii* Taub, a species of *Pterocarpus* in the *family Fabaceae* was investigated using weight loss and hydrogen evolution techniques with the aim of determining its inhibition potentials in alkaline medium, investigate the effect of temperature on the corrosion of mild steel, study the effect of different concentrations of ethanol extract of *P. soyauxii* at different temperatures, calculate thermodynamic parameters and propose the mechanism of corrosion inhibition of mild steel in Na_2CO_3. Results obtained revealed that inhibition efficiency maintained a direct proportional relationship with inhibitor concentration, but an inverse relationship with temperature. Values of inhibition efficiency from the two methods showed no significant difference (P = 0.05) within the range under review. Langmuir adsorption model was found to best suit the adsorption of the inhibitor molecules on the surface of mild steel. Values of thermodynamic parameters revealed that the corrosion reaction is exothermic, spontaneous and followed the mechanism of physical adsorption. The inhibitor exhibited an appreciable percentage of inhibition at optimal inhibitor concentration. The results suggest that *P. soyauxii* can actually be used as a green corrosion inhibitor.

Keywords: *Pterocarpus soyauxii*, inhibition efficiency, adsorption, exothermic, Langmuir

INTRODUCTION

Corrosion as a highly destructive process negatively affects the performance of metallic materials applied in many construction sites. Corrosion is a natural phenomenon commonly defined as the deterioration of metal surfaces as a result of their reaction with the surrounding environmental conditions. The consequences of corrosion are quite diverse and pose a great problem in the industries, construction and other civil services.

It has been observed that mild steel corrodes in different concentrations of aggressive media resulting to a decrease in the original weight of the coupons. The corrosion is attributed to the presence of water, air and ions which accelerate the corrosion process. The anode dissolution which is initiated on the metal surface as the reaction site is as shown below.

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

The main tactic applied in mitigating the corrosion of mild steel is to separate the metal from corrosive environment, and this can be achieved using corrosion inhibitors. A corrosion inhibitor is a substance which when added in small concentrations to an environment, effectively reduces the corrosion rate of a metal exposed to it.

Recently, the use of chemical inhibitors such as Chromates, Silicates and organic amines has come under severe criticism due to the environmental problems associated with it. Attention has shifted to naturally occurring substances because they are environmental friendly. Plant extracts are considered to be rich in naturally synthesized chemical compounds which are not only biodegradable, non-toxic, cheap but are also renewable. Much of these natural products have been used by many researchers as corrosion inhibitors for different metals in various environments and optimum concentrations were reported for all of them (Avwiri and Igho, 2003; Gunasekaran and Chauhan, 2004; El Eter *et al*., 2005; Abdel-Gaber *et al*., 2006, 2008; Oguzie, 2007; Odiongenyi *et al*., 2009; Yende *et al*., 2010; Singh *et al*., 2011; Shyamala and Kasthuri, 2011). The data obtained from the various studies showed that plant extracts could actually serve as effective inhibitors for corrosion. It has been established that the mechanism of corrosion inhibition is via adsorption of the inhibitor molecules on the corroding metal surface and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of both the inhibitor and the adsorption layers formed under particular conditions (Eddy *et al*., 2012). Many research groups have done similar work and returned physiosorption as the mechanism of adsorption of inhibitors on the surface of mild steel , while Langmuir isotherm passed as the best adsorption model (Obot *et al*., 2011; Eddy *et al*., 2012; Rajendran *et al*., 2013; Onuegbu *et al*., 2013).

As a contribution to the growing interest in environmental friendly green corrosion inhibitors, this present study seeks to investigate the inhibiting effect of ethanol extracts of *Pterocarpus soyauxii* leaves on the corrosion of mild steel in alkaline medium.

The genus *Pterocarpus* which is tropically and sub-tropically distributed belongs to the family Leguminosae. There are about 60 species of the genus of which 20 of these are found in Africa in countries such as Nigeria, Cameroon, Sierra Leone and Equatorial Guinea. The leaves of *Pterocarpus soyauxii* are used for soup making in the South Eastern part of Nigeria. Some tribes in the Eastern and Southern Nigeria use the leaf extracts in the treatment of headaches, pains, fever, convulsions and respiratory disorders and as antimicrobial agents (Ogukwe *et al*., 2004). Notable phytochemical constituents of ethanol extract of *P. soyauxii* are saponins, phenols, alkaloids, flavonoids, tannins, cyanogenic glycosides, steroids (Ndukwe and Ikpeama, 2013).

MATERIALS AND METHODS.

Materials

Materials used for the study were mild steel sheets of composition (% w/w) Fe (98.86), Mn (0.6), P (0.36), C (0.15) and Si (0.03). The sheet was mechanically pressed cut into different coupons, each of dimension 4x3x0.11 cm. Each coupon was degreased by washing with ethanol, rinsed with acetone and allowed to dry in air before they were preserved in desiccators. All reagents used for the study were Analar grade and double distilled water was used for their preparation.

Extraction of plant

The leaves of *Pterocarpus soyauxii* were collected from several sites within Aba North L.G.A. of Abia State and were identified in the Biology/Microbiology Department of Abia State polytechnic Aba. The leaves were ground after air-drying. 100 g of the ground leaves were soaked in ethanol for 48 hours. The Sample was cooled and filtered. The filtrate was further subjected to evaporation at 352K in order to leave the sample free of the ethanol. The slurry extract so obtained was used in preparing different concentrations of the inhibitor by dissolving 0.1 g, 0.2 g, 0.3 g, 0.4 g and 0.5 g of the extract in 1 L of 1.0 M Na_2CO_3 and 1 L of 2.5 M Na_2CO_3 for use in gravimetric and gasometric analyses, respectively.

Gravimetric Analysis

Gravimetric study using the ethanol extract of *Pterocarpus soyauxii* leaves was done by dipping the pre-cleaned mild steel into 20 mL of the test solution maintained at 303 and 333 K in a thermo stated bath. The weight loss was determined by retrieving the mild steel coupons at 1hr interval progressively for 7 hrs. Prior to measurement, each retrieved coupon was immersed in a solution of 20% HCl containing 200 g/L of Zinc dust to terminate the corrosion reaction, scrubbed with brittle brush several times and dried in acetone. The difference in weight was taken as the weight loss of the steel. A control experiment was equally set up by considering the weight loss of mild steel coupons in various concentrations of Na_2CO_3 in the absence of the inhibitor. From the weight loss, the inhibition efficiency of the inhibitor (I %), degree of surface coverage (θ) and corrosion rate (CR) of the steel were calculated using equations 1, 2 and 3 respectively.

$$\% I = \left(\frac{1 - W_2}{W_1}\right) * 100 \quad (1)$$

$$\theta = \frac{\% I}{100} \quad (2)$$

$$CR = \frac{W}{At} \quad (3)$$

Where % I is the inhibition efficiency of the ethanol extract of *P. soyauxii*, CR is the corrosion rate of steel in $gcm^{-2}hr^{-1}$, W_1 and W_2 are the weight losses of steel in the absence and presence of the inhibitor, respectively. W is the difference in weight in (g) before and after immersion, (i.e. $W = W_2 - W_1$), t is the period of immersion in hours and A is the area of the steel coupon in square cm^2.

Hydrogen evolution was carried out at 303 and 333 K as described in literature (Oguzie *et al.*, 2006; *Umoren et al.*, 2006a, 2007).

RESULTS AND DISCUSSION

Figure 1 depicts the variations of weight loss against time for mild steel in the test solutions at 303 K clearly shows a reduction in weight loss of the metal coupons in the presence of the inhibitor compared to the uninhibited solution (blank), indicating that ethanol extract of *Pterocarpus soyauxii* inhibited the corrosion of mild steel in Na_2CO_3. The inverse proportional relationship between weight losses of the mild steel coupons and the concentrations of the inhibitors is also revealed. At higher temperature, similar trend was observed though with greater values of weight loss.

Figure 2 shows variations of volume of hydrogen gas evolved with time during the inhibition of the corrosion of mild steel in 2.5 M Na_2CO_3 with various concentrations of *Pterocarpus soyauxii* leaf extracts at 303 K. The Figure revealed a decrease in the volume of hydrogen gas evolved with different concentrations of *P. soyauxii* extracts compared to the blank, showing that different concentrations of *P. soyauxii* extract inhibited the corrosion of mild steel in 2.5 M Na_2CO_3. Similar observations were equally revealed at 333 K.

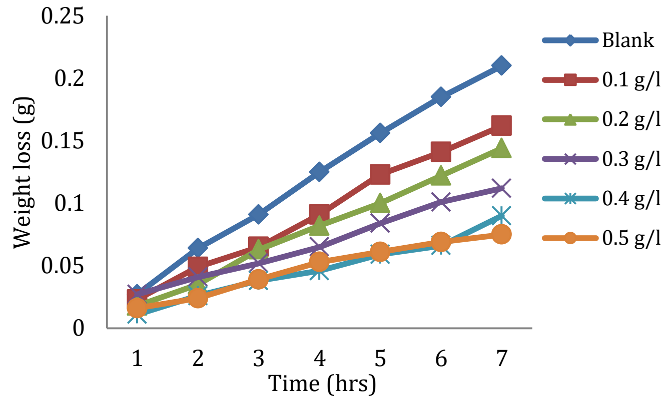

Figure1: Graph of corrosion (weight loss) of mild steel in 1.0 M Na_2CO_3 at 303 K with time

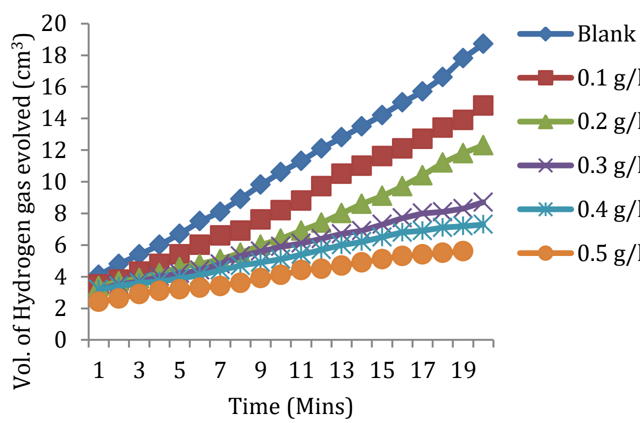

Figure 2: Graph of volume of hydrogen gas evolved of mild steel in 2.5 M Na_2CO_3 at 303 K with time

Effect of Inhibitor Concentration

The plot of corrosion rate against inhibitor concentration for the corrosion of mild steel in 2.5 M Na_2CO_3 at 303 K and 333 K is shown in Figure 3. The result showed that the corrosion rate decreases as the concentration of the inhibitor increases at both temperatures. The result also showed that the leaf extract retards the corrosion rate of the mild steel in the test solutions with better efficiency at lower temperature. This assertion is clearly shown in Figure 4, where the inhibition efficiency of *P. soyauxii* at 303 K was progressively higher than that at 333 K at the various concentrations under review (0.1-0.5 g/L).

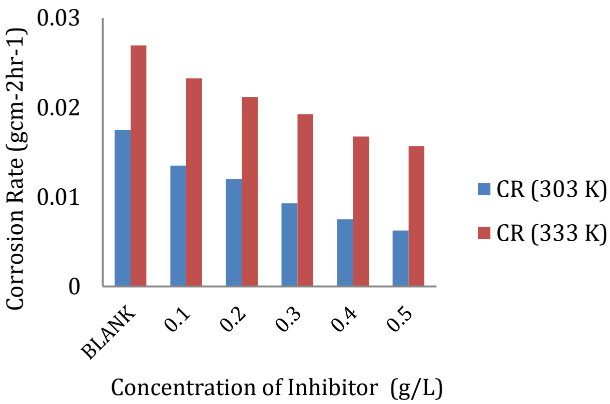

Figure 3: Graph of corrosion rate for mild steel coupons in 2.5 M Na_2CO_3 at different temperatures.

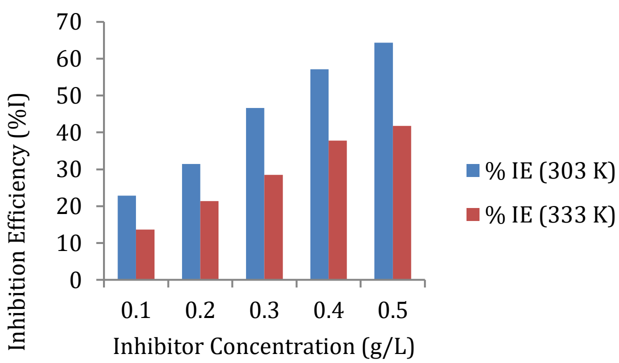

Figure 4: Graph of Inhibition Efficiency for mild steel coupons in 2.5 M Na_2CO_3 at different temperatures.

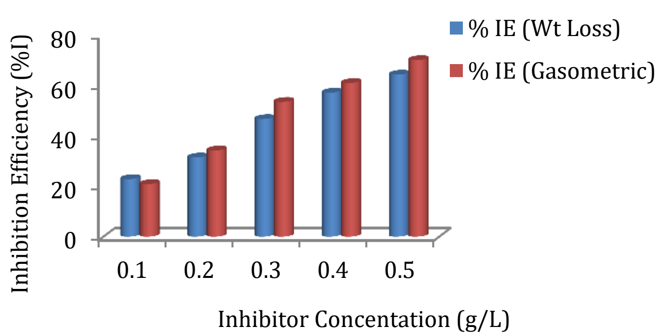

Figure 5: Graph of Inhibition Efficiency for mild steel coupons in Na_2CO_3 at 303 K for Weight loss and Gasometric methods.

Table1 shows values of inhibition efficiency (%I) and corrosion rates (CR) of *Pterocarpus soyauxii* (PS) leaf extract on mild steel surface in 2.5 M Na_2CO_3 at 303 and 333 K. From the table, the inhibition efficiency increased with increase in the concentration of PS, but decreased with increase in temperature. Also the corrosion rate of mild steel decreased as the concentration of PS increased but increased with increase in temperature, suggesting physical adsorption of the inhibitor molecules on the surface of mild steel as the inhibitor molecule could be said to be desorbed from the mild steel surface at elevated temperature (Eddy, 2008). Inhibition efficiency values from weight loss and hydrogen evolution methods showed no significant difference (P = 0.05) within the temperature range under review, indicating that the inhibitor can be used both for short and long term inhibitions.

Mechanism of inhibition

The phytochemical composition of the leaf extract of *Pterocarpus soyauxii* reveals that it contains compounds such as saponins, phenols, alkaloids, flavonoids, tannins and steroids that can adsorb on the metal surface via the lone pair of electron present in the heteroatom which abound in these constituents (Oguzie, 2007; Ndukwe and Ikpeama, 2013). This could be thought to create a barrier for charge and mass transfer leading to a decrease in the level of interaction between the metal surface and the corrosive environment. This in turn decreases the corrosion rate of the metal. The discharge of H^+ and dissolution of metal ions are blocked essentially by the formation of a film layer on the metal surface. The resulting protonated constituent molecules are adsorbed physically and high inhibition is likely to occur. Compounds containing heteroatoms e.g. (N, S and O), behave in similar manner to inhibit corrosion (Ajmal *et al*., 1994; Moretti *et al*., 2004; Shyamala and Kasthuri, 2011).

Table 1: Values of inhibition efficiency (%I) and corrosion rates at 303 and 333 K obtained from Gravimetric method, and inhibition efficiency (%I) at 303 K obtained from Gasometric method for the corrosion of mild steel in Na_2CO_3 solution containing different concentrations of *Pterocarpus soyauxii leaf* extracts.

	Weight loss				Gasometric
Conc. of (PS) (g/L)	**%I (303 K)**	**%I (333 K)**	**CR ($gcm^{-2}h^{-1}$) 303 K**	**CR ($gcm^{-2}h^{-1}$) 333 K**	**% I (303 K)**
Blank			0.0175	0.0269	
0.1	22.86	13.62	0.0135	0.0233	20.86
0.2	31.42	21.36	0.0120	0.0212	34.22
0.3	46.66	28.48	0.0093	0.0193	53.48
0.4	57.14	37.77	0.0075	0.0168	60.96
0.5	64.29	41.80	0.0062	0.0157	70.05

Thermodynamic and adsorption considerations.

The modified Arrhenius equation was used in calculating the activation energy for the corrosion reaction of mild steel in the presence and absence of different concentrations of ethanol extract of *Pterocarpus soyauxii*.

$$\log\frac{CR_2}{CR_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad (4)$$

Where E_a is the activation energy, CR_1 and CR_2 are values of corrosion rates at temperatures T_1 and T_2 and R is the universal gas constant.

Calculated values of E_a are shown in Table 2. The Ea value in the absence of the inhibitor is 11.40 KJ/mol which is lower than the values obtained for the inhibited systems. The values in the presence of the inhibitor ranged from 14.47- 24.63 KJ/mol with a mean of 18.99 KJ/mol, supporting the mechanism of physical adsorption. For physical adsorption, the value of Ea should be less than 80 KJ/mol (Ebenso, 2003a,b, 2004; Sheatty *et al*., 2006; Eddy and Ebenso, 2008).

The heat of adsorption of *P. soyauxii* on the surface of mild steel was calculated using equation (5).

$$Q_{ads} = 2.303R\left(Log\left[\frac{\theta_2}{1-\theta_2}\right] - Log\left[\frac{\theta_1}{1-\theta_1}\right]\right) \times \frac{T_1T_2}{T_2-T_1} \text{ kjmol}^{-1} \quad (5)$$

Where θ_2 and θ_1 are the degrees of surface coverage at the temperatures T_2 and T_1 respectively and R is the gas constant.

The heat of adsorption (Q_{ads}) should approximate the enthalpy change, since the experiment was carried out at constant pressure (Umoren *et al*., 2006a,b). Calculated values of Q_{ads} were negative as recorded in Table 2 and ranged from -14.63 to -25.70 KJ/mol with a mean of -20.25 KJ/mol, indicating that the adsorption of *P. soyauxii* on mild steel surface is exothermic. The negative values could be attributed to the fact that the adsorption and hence the inhibition efficiency decreases with increase in temperature. Other authors have equally reported similar observations (Bhajiwala and Vashi, 2001; Eddy and Ebenso 2008).

Several attempts were made to fit data obtained from degrees of surface coverage Θ at various concentrations of the inhibitor into different adsorption isotherms (Eddy and Ebenso, 2011). All the isotherms can be represented as follows:

$$f(\Theta, x)\exp(-2a\Theta) = KC \quad (6)$$

Where f(Θ, x) is the configuration factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm, Θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, x is the size ratio, a is molecular interaction parameter and K is the equilibrium constant of the adsorption process.

Langmuir adsorption model which can be written as shown in equation (7) was found to best describe the adsorption of ethanol extract of *P. soyauxii*.

$$Log\left(\frac{C}{\Theta}\right) = LogC - LogK \quad (7)$$

Also equation (8) which relates K (Equilibrium constant of adsorption) to free energy of adsorption was used in calculating values of free energy.

$$\Delta G^0_{ads} = -2.303RTLog(55.5K) \quad (8)$$

The Langmuir isotherm plot for the adsorption of ethanol extract of *P. soyauxii* on mild steel surface is shown in Figure 6. The applicability of Langmuir adsorption isotherm to the adsorption of *P. soyauxii* on mild steel is a confirmation of the formation of multi-layer adsorption, where there is no interaction between the adsorbate and adsorbent (Eddy and Ebenso, 2008).

From the results, it was observed that Langmuir adsorption isotherm was best applicable at 303 K (R^2 = 1.0000). This is a confirmation that the adsorption behaviour of the inhibitor is strongly influenced by temperature. The value of ΔG^o_{ads} which are negatively less than the threshold value of (-40 KJ/mol) indicate that the adsorption of the inhibitor is spontaneous and also confirms the mechanism of physical adsorption.

Table 2: Kinetics and thermodynamic parameters for the adsorption of ethanol extract of *Pterocarpus soyauxii* on the surface of mild steel.

C(g/l)	Ea(KJmol^{-1})	Qads (KJ/mol)
Blank	11.40	-
0.1	14.47	-16.92
0.2	15.09	-14.63
0.3	19.36	-22.01
0.4	21.38	-22.01
0.5	24.63	-25.70

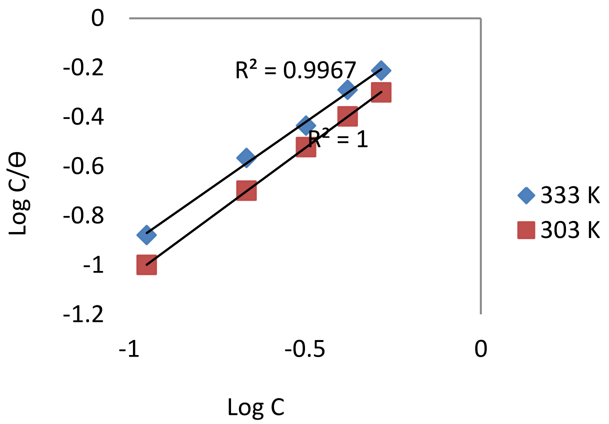

Figure 6: Langmuir plots for the adsorption of *Pterocarpus soyauxii* on mild steel surface.

Table4: Langmuir adsorption parameters for the adsorption of *Pterocarpus soyauxi* on the surface of mild steel.

	Temp	Log K	Slope	ΔGads (KJ/mol)	R^2
Langmuir	303K	-1.15	1.0101	-3.45	1.0000
	333K	-0.98	1.0097	-4.87	0.9967

CONCLUSION

This study on the corrosion inhibition potentials of *Pterocarpus soyauxii* Taub leave extracts revealed that various concentrations of the ethanol extract of *P. soyauxii* were capable of inhibiting the corrosion of mild steel in Na_2CO_3. The efficiency of inhibition of the extract was found to increase with increase in concentrations of *P. soyauxii*, but decreased with increase in temperature. The activation energies of the inhibited systems were higher than that of the uninhibited system, suggesting physiosorption mechanism. This trend in the mechanism of inhibition was further supported by the values of heat of adsorption. Langmuir adsorption model was found to characterize the adsorption of *P. soyauxii* on mild steel surface. Ethanol extract of *P. Soyauxii* can actually be used as a green corrosion inhibitor for the corrosion of mild steel in Na_2CO_3 within the temperature range under review. This can actually help in the elimination of toxicants associated with conventional inhibitors such as inorganic and synthesized inhibitors.

CONFLICT OF INTEREST

None declared.

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