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Research Article

CORROSION INHIBITION BEHAVIOUR OF *EMILIA SONCHIFILIA* LEAVES EXTRACT AS A GREEN CORROSION INHIBITOR FOR MILD STEEL IN HYDROCHLORIC ACID MEDIUM

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ABSTRACT

The corrosion of mild steel in HCl medium was studied using the leave ethanol extract of *Emilia sonchifilia* (ES). The methods used were Gravimetric at 30^oC and 60^oC, Thermometric and Gasometric. The results obtained showed that the rate of corrosion of mild steel increases with increase in concentration of the acid (1.0M-2.5.0M) and also with temperature increases from 30^oC to 60^oC. ES extract of different concentrations (0.1-0.5g/l) were found to inhibit corrosion as the concentrations of the ES extract increases with increase in the temperatures. ES obeyed the Langmuir and Tempkin adsorption isotherms. Mechanism of physical adsorption was proposed from the values ΔG^o, ΔH and Ea obtained. Inhibition efficiencies (I%) and surface coverage (θ) were also calculated, all indicated that ES extract is a good corrosion inhibitor.

Key Words: *Corrosion, Inhibition, Mild Steel and Emilia Sonchifolia*

INTRODUCTION

Mild steel is the cheapest and most versatile form of steel and serves every application which required a bulk amount of steel. Mild steel is used in construction of electrical devices, in car manufacturing, oil and gas, and aircraft industries. It is also used in chemical and allied industries for handling of acid, alkalis, and salt solution (Bilgic Caliskan, 2001). Mild steel is susceptible to corrosion attack in humid air and when it comes in contact with acid solution, during acid cleaning, transportation of acid, storage of acids and other chemical processes because of high amount of carbon it contain (Saratha and Vasudha, 2009). US government spends billions of dollars every year because of the menace of corrosion and the same huge cost is applicable to every industry that is using mild steel in production of goods all over the world. In other to minimize this great loss of resources, the use of corrosion inhibitor has become an answer to the solution of this problem. Corrosion inhibitors are chemical compounds which added in small quantity to the corrosive medium reduces the rate of corrosion attack on the metal or alloy Corrosion inhibitor can be organic or inorganic compound. Chromate, cadmium, phosphate, lead based compounds are some of the inorganic compound that inhibit corrosion but were found to be toxic and harmful to the environment (Meligi, 2010).These pure synthetic chemicals are costly, some of them are not easily biodegradable and their disposal creates pollution problems. Recently, organic inhibitors has received much attention because they are cheap, easily available, biodegradable and environmentally friendly. Plant products are organic in nature and some of the constituents including tannin, organic amino acid, alkaloid, and pigments are known to exhibit inhibitory actions. Equally they can be extracted by simple procedure with low cost (Abdel-Gabar, 2009; Raja and Sethuraman 2008). Many plant extracts have been used as corrosion inhibitors such as aqueous extract of *kalmegh (Andrographis paniculata)* (Ambrish *et al.*, 2010). *Capparius deciduaina* (Arora *et al.*, 2007) black pepper extract (Quraish *et al.*,2009) exudates from *Pachylobus edulia* (Umoren *et al.*,2008a) gum exudates from *Acacia seyal var* (Saratha *et al.*, 2009), *citrus aurantiifolia* (Patel *et al.*, 2009), *Nyctanthes arbortistis* (Saratha and Vasudha, 2009), *Bauhinia purpurea* (Saratha and Vasudha) *and Emblica officinalis (*Buchweishaija and Mhinzi, 2007). As a contribution to the current interest of environmentally friendly, green corrosion inhibitors, the present study investigated the inhibitive behaviour of leave extracts of *Emilia sonchifolia* (ES). *Emilia sonchifolia* is a weed that grows on a farm lands. It can be found in forest in many part of Nigeria. It is believed to be a medicinal plant that cures boils, diarrhea, cold and flu infections, ear problems and cataract (Ajiwe *et al.,* 2008).

MATERIALS AND METHODS

Preparation of Emilia sonchifolia leaves extracts

1500g of leaves of ES was air dried in a shade for 8-12 days. It was thereafter ground into powder. 431g of the finely powdered dried material was taken in 1000ml round bottom flask and enough quantity of ethanol was added as a solvent for the extraction. The round bottom flask was covered with a stopper and left for 48hrs. Then the resulting paste was refluxed for 5hrs, and it was filtered. The solvent was removed by concentrating the materials to about 20%. From these, 0.1 – 0.5g/l concentration was made.

Specimen Preparation

Mild steel of 1.44mm thickness was obtained locally and was mechanically cut into coupons of 4 x 4 x 0.144cm and 2 x 3 x 0.144cm. A small hole was drilled at one end of the coupons for easy hooking. The coupons were used as a cut without further polishing. They were degreased in absolute ethanol, dried in acetone and stored in a desiccator.

Test Solution Preparation

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

Weight Loss Method

This experiment was done at a temperature 30^oC and 60^oC. In this experiment, the 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 thermostated water bath. The coupons were removed each day i.e. at 24h 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 (Umoren *et al.,* 2006a). The differences in weight of the coupons were taken as the weight loss which was used to compute the corrosion rate given by;

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

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 the ES was calculated using the expression:

$$I\% = (W_1 – W_0 / W_1) \times 100 \quad (2)$$

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

$$\theta = (W_1 – W_0) / W_1 \quad (3)$$

Thermometric Method

The procedure for determining this has been described by (Ebenso, 2003a, Ebenso, 2003b and Umoren *et al.,* 2006b) . The mild steel of 2x 3 x 0.14cm were used here. Volume of the test solution was at 100ml reagent. From the rise in temperature of the system per minutes, the reaction number (RN) was calculated using this:

$$RN\ (^0C\ min^{-1}) = \frac{Tm-Tt}{t} \quad (4)$$

Where T_m is the maximum temperature attained by the system, T_t is the initial temperature and t is the time (mins). Inhibition efficiency I(%) of the Es inhibitor can as well be calculated using:

$$I\%= \frac{RN-RNwi}{RNaq} \times 100 \quad (5)$$

Where RNaq is the RN in the absence of inhibitor (ES) while RNwi is the RN in the presence of inhibitor (ES).

Gasometric Method

Mild steel of 2 x 3 x 0.144cm were used here and this experiment were carried at 30°C and 60°C.The procedure for this experiment has been documented in literature (Umoren *et al.*, 2008b). From the volume of hydrogen evolved per minute inhibition efficiency I% and degree of surface coverage (θ) were calculated using equation 6 & 7

$$I\% = \left(1 - \frac{V1Ht}{V0Ht}\right) \times 100 \quad (6)$$

$$\theta = I - \frac{V1Ht}{V0Ht} \quad (7)$$

Where V^1_{Ht} and V^0_{Ht} are the volume of H_2 gas evolve at time `t` for inhibited and uninhibited solution respectively.

RESULTS AND DISCUSSION

Weight Loss Method (Gravimetric)

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

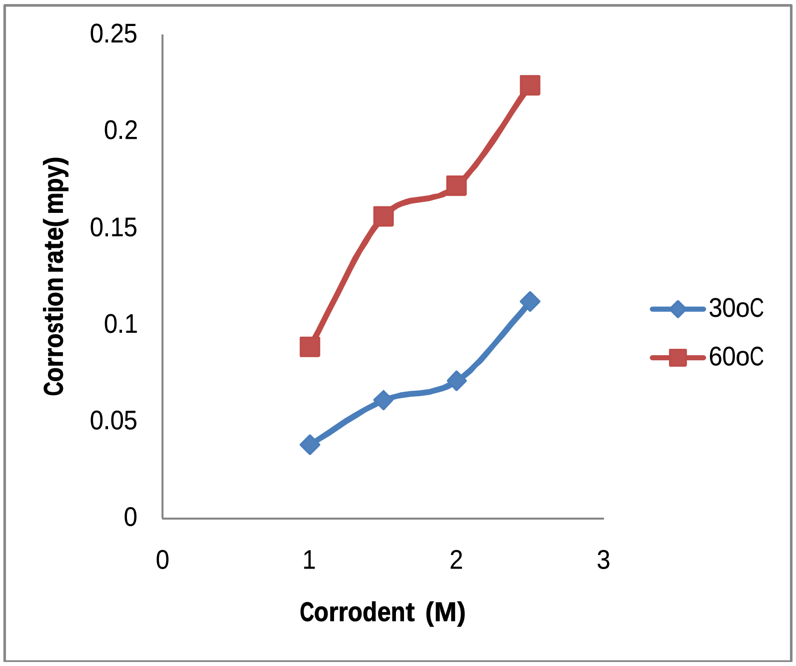

Figure 1: plot of corrosion rate against corrodent concentration for mild steel corrosion of different concentration

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^{0}C and 60^{0}C . The figure revealed that the corrosion rate decreases as the concentration of the inhibitor increases at 30^{0}C and 60^{0}C.

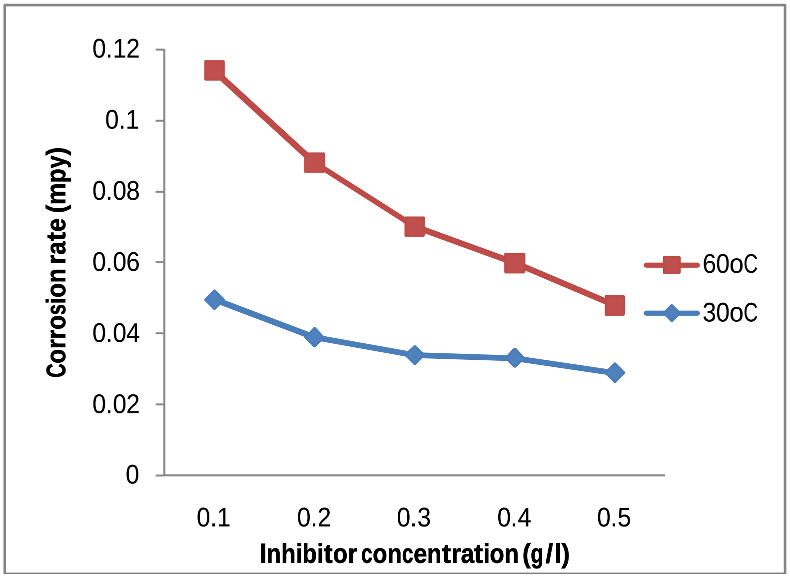

Figure 2: Plot of corrosion rate against inhibitor concentration for the corrosion of mild steel in 2.5M HCl at 30°C and 60°C

Fig.3 and 4 revealed the variation of weight loss with time in the absence of inhibitor, at 1.0M-2.5M at 30^{0}C and 60^{0}C and in the presence of different concentration, of ES inhibitor at 30^0 and 60°C. It was obtained from the plot that weight loss of mild steel decreases as the concentration of the ES extract increases compared to the blank experiment. This was also as a result of the inhibitive action of the ES extract on the mild steel.

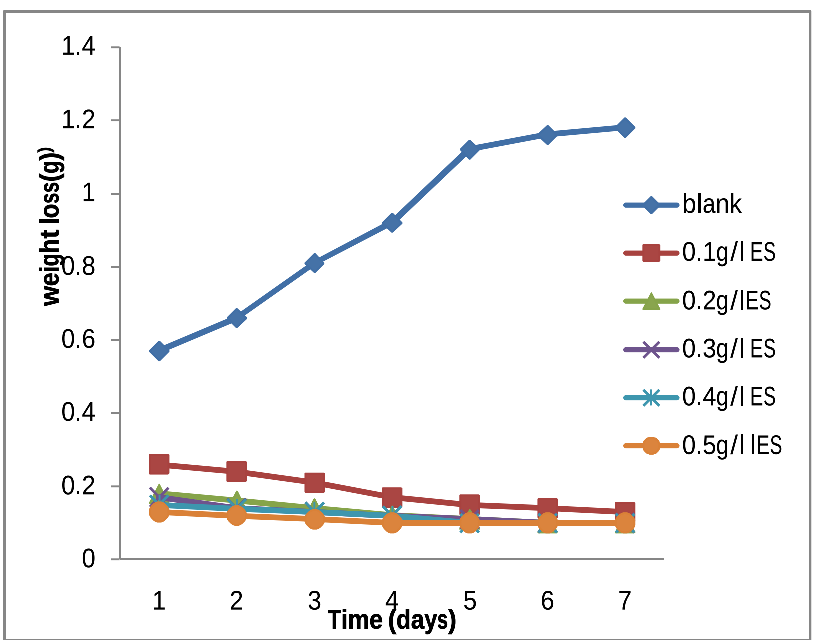

Figure 3: Variation of weight loss with time for mild steel corrosion in 2.5M HCl in presence and absence of ES extract at 30°C

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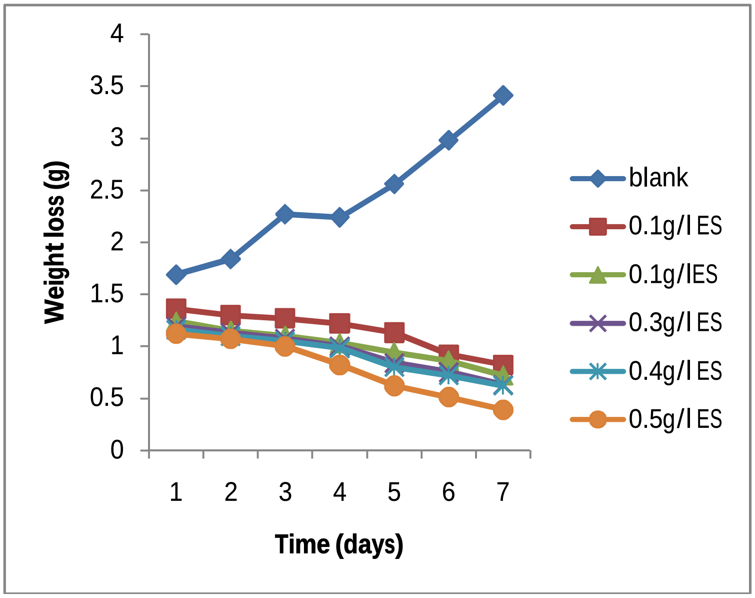

Figure 4: Variation of weight loss with time for mild steel corrosion in 2.5M HCl in presence and absence of ES extract at 60^oC

Thermometric Method

Table 1 revealed the reaction number and inhibition efficiency (1%) of mild steel in 2.5M HCl. It could be emphasized from Table 1 that reaction number decreases as the concentration of the ES extract increases. From Table 1, it was inferred that inhibition efficiency increases as concentration of ES extract increase. These indicated that the molecule of the ES extract had adsorbed on the surface of the mild steel thereby preventing further corrosion attack.

Table 1: **Calculated values of inhibition efficiency and reaction number at various concentration of ES extract from thermometric method**

Concentration of inhibitor in g/l	Reaction number(^{o}CMin^{-1})	Degree of surface coverage (θ)	Inhibition efficiencies (I%)
0.1	0.0375	0.4231	42.31
0.2	0.0320	0.5071	50.71
0.3	0.0270	0.5777	57.77
0.4	0.0249	0.6169	61.69
0.5	0.0223	0.6569	65.69

Gasometric Method

Fig.5 and 6 showed the variation in volume of H_2 evolved with time at 30^{0}C and 60^{0}C with different concentrations of the ES extract. It could be observed from the plot that volume of H_2 evolved increases with time. The rate of hydrogen evolved decrease as the concentration of ES extract increases compare with the blank. This result agreed with weight loss, and thermometric method result that ES extract is a good inhibitor for mild steel.

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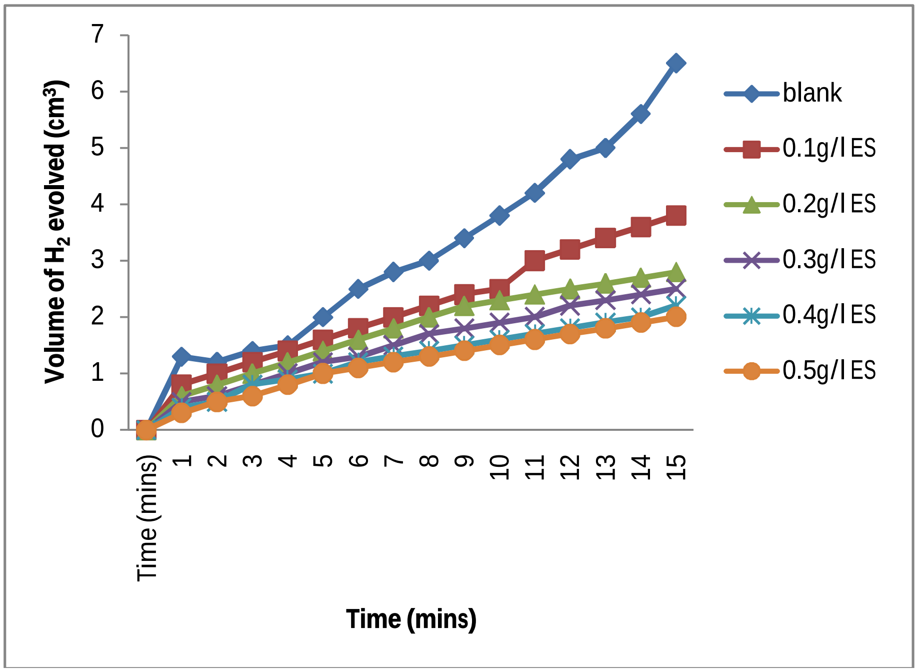

Figure 5: A plot of volume of hydrogen evolved with time for the corrosion of mild steel in 2.5M HCl in the presence and absence ES extract at 30°C

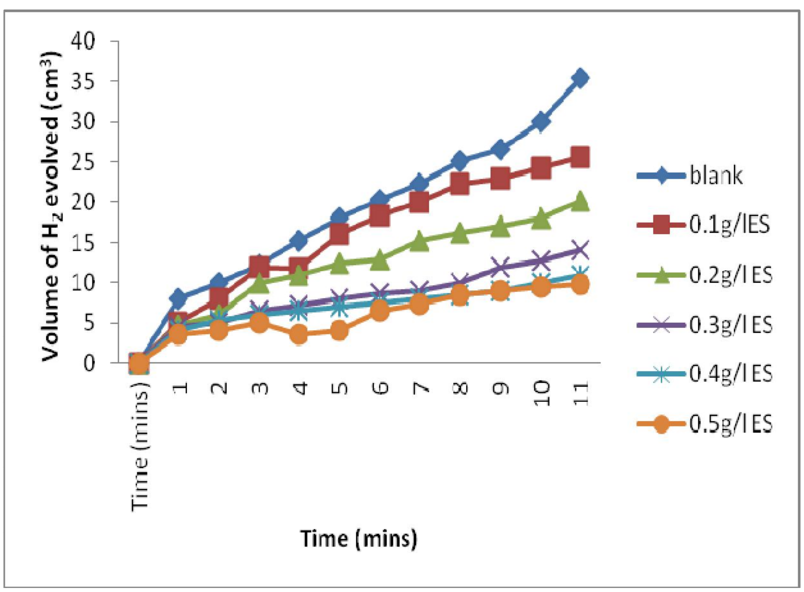

Figure 6: A plot of volume of hydrogen evolved with time for the corrosion of mild steel in 2.5M HCl in the presence and absence ES extract at 60°C

Adsorption Consideration

Fig.7, depict the plot of inhibition efficiency against inhibitor concentration at 30^{0}C and 60^{0}C for the ES extract. Inspection of the fig. 7 showed that inhibition efficiency increases with increase in ES concentration and with decrease in temperature. Increase in inhibitor efficiency with decrease in temperature sug-

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gested of physical adsorption mechanism. The character of adsorption of ES extract was further elucidated from degree of surface coverage (θ) (from weight loss data). Assumption of Langmuir adsorption isotherm can be expressed with equation (7) (Agrawa *et al.*,2003 and Umoren *et al.*,2006c).

$$C/\theta = C + {}^{1}/_{k} \quad (7)$$

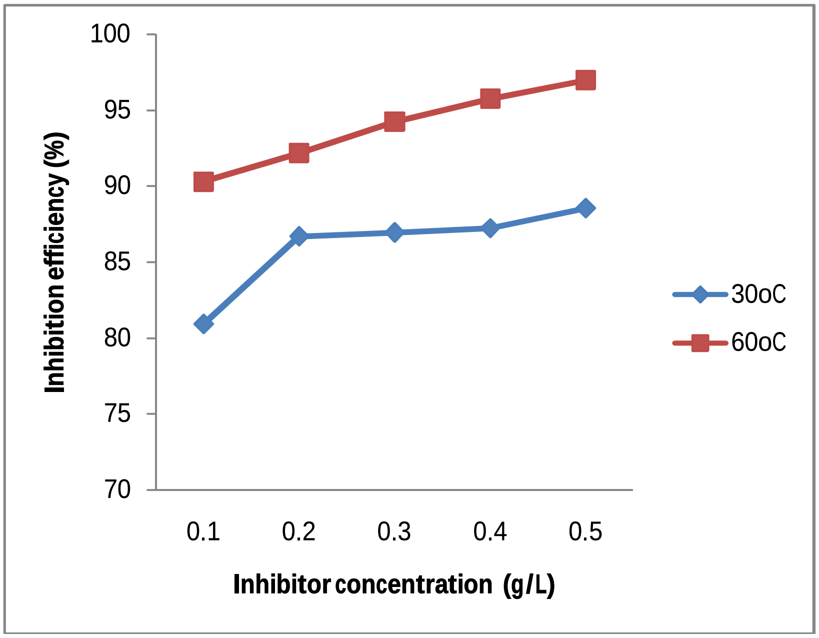

Figure 7: The plot of inhibition efficiency against inhibitor concentration at 30°C and 60°C

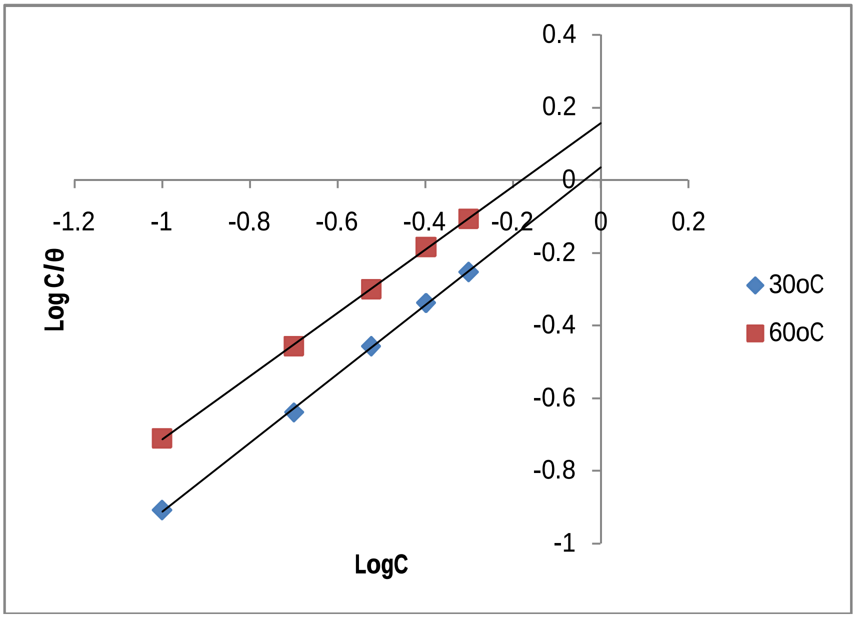

Figure 8: Langmuir adsorption isotherm plot of c/θ versus C at 3°C and 60°C

Taking the logarithm of equation 7

Log C/θ = log C – log K where C is the concentration of the inhibitor in electrolyte, θ is the degree of surface coverage of the inhibitor ES and K is the equilibrium constant. A plot of (C/θ) versus C fig. (8) were linear indicating Langmuir adsorption isotherm .

Fig. 9, Shows Tempkin adsorption of ES extract of mild steel corrosion at 30^{o}C and 60^{0}C

Tempkin adsorption isotherm is known with this equation (Abdullah, 2004; Umoren, 2006d ; Umoren *et al.*,2004)

$$\theta = \frac{-2303 \log K}{2a} - \frac{2303 \log C}{2a} \quad (8)$$

Here, a plot of θ versus log C was made and was linear and fitted into Tempkin Adsorption Isotherm.

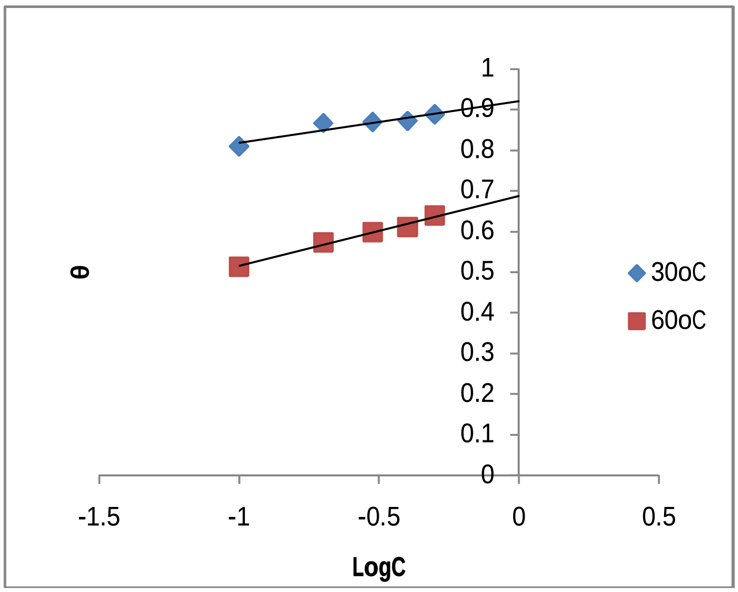

Figure 9: Tempkin adsorption isotherm plot for mild steel corrosion θ versus log C

Thermodynamics Studies

The value of activation energy Ea was calculated with Arrhenus equation.

$$\text{Log} \frac{CR2}{CR1} = \frac{Ea}{2.303R} \left(\frac{1}{T1} - \frac{1}{T2}\right) \quad (10)$$

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 ES. The values of heat of adsorption, ΔH_{ads} were calculated using equation (11)
(Ebenso, 2003b).

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

Where θ_1 and θ_2 are degree of surface coverage at temperatures, T_1 and T_2 respectively. Table 2: enumerated the values Ea and ΔH_{ads} at different concentrations of inhibitor, the values of Ea were found to increase with increase in the concentrations ES inhibitor. This showed that the ES was physically adsorbed on the surface of the mild steel preventing further corrosion attack due to the phytochemical constituents it contained. The values of ΔH_{ads} were negative throughout suggesting exothermic reaction. The equilibrium constant of adsorption of ethanol extract of ES is related to the free energy of adsorption (ΔG_{ads}) according to the following equation 12

$$\Delta G_{ads} = -2.303RT\log(55.5K) \qquad (12)$$

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 Tempkin isotherm were used to compute values of ΔG_{ads} according to equation 12 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 ES on the surface of mild steel is spontaneous and follows physical adsorption mechanism (Ayssar *et al.*,2010 and Rani and Selvaraj, 2010).

Table 2: Calculated Values of Activation Energy And Heat Of Adsorption

Concentration of inhibitor in g/l	Ea(KJ/mol)	ΔH_{ads}(kJ/mol)
0.1	50.87	-271.5
0.2	56.16	-44.12
0.3	56.39	-41.85
0.4	56.87	-41.14
0.5	58.25	-36.55

Table 3: Langmuir and Tempkin Adsorption Isotherm Parameters for Adsorption Of Ethanol Extract of ES

Temperature (°C)	Log K	Slope	ΔG_{ads} (KJ/Mol)	R^2
	Langmuir			
30°C	0.448	0.6239	-8.096	0.9548
60°C	0.239	0.7818	-7.152	0.9735
	Tempkin	**A**		
30°C	0.9162	4.8676	-9.899	0.8536
60°C	0.8626	2.9034	-10.712	0.9662

Conclusions

ES extract showed inhibitive effect on corrosion of mild steel in acidic environment.

Inhibition efficiency increases with an increase in inhibitor concentration as a result of the phytochemical constituents of the ES. Extract.

The adsorption of ES extract followed Langmuir and Tempkin, adsorption isotherms.

The mechanism of physical adsorption was proposed from the calculated values of Ea, ΔH_{ads}, and ΔG_{ads}, obtained.

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