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RESEARCH ARTICLE

CORROSION INHIBITORY CHARACTERISTICS OF *JATROPHA CURCAS*ON ZINC ALLOY IN 1.5M HCL SOLUTION

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ABSTRACT

This work investigated the corrosion behaviour of *Jatrophacurcas* (JC) crude leave extract on zinc metal in the presence of 1.50 MHydrochloric acid solution at 28°C by hydrogen evolution (Gasometric) method. The results revealed that JC effectively inhibited the induced corrosion of zinc in the HCl solution. Inhibition efficiency increases as in extract concentration increases with optimum efficiency at 50v/v%. Corrosion rate retarded with increase in extract concentration. Specific reaction constant and Half-life of metal in the media are 6.251726928 $x10^{-8}$ and 0.110872913 $x10^{8}$ minutes respectively. Four adsorption isotherms were employed. Langmuir isotherm best explains the physical adsorption interface mechanism between the extract and its adsorbed layers formed on the zinc surface with a correlation coefficient (R^2) of 0.990. Free energy of adsorption of - 5.87KJmol^{-1} indicated a spontaneous process of physical adsorption of the extract on the zinc surface. Surface morphology were studied with Scanning Electron Microscope (SEM) and Electron dispersive X-ray spectroscopy (EDX) which revealed the protection of the internal grains of the metal from dissolution into corrodent provided by the adsorbed film the extract.

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INTRODUCTION

The response of nature to various ecological distortions carried out by man as led to effective deterioration of materials (especially metals) which are in constant interaction with the environment. These materials are seen to change form (that is degraded, corrode or reverting to more stable natural state) as they interact with surrounding chemicals emanating from human activities (Ajanaku *et al*., 2014; Siyanbola *et al*., 2013).Metal corrosion process has affected various operations units in the industries resulting to huge operational losses (Barbara and Robert, 2006). Corrosion affect water bodies (such as sea and river) when pipes meant for conveying useful industrial products or otherwise in the water bodies corrodes and appropriate maintenance are not carried out, leaks will gradually set in and the survival of the ecosystem will become threatened by fire, capital loss, explosion and loss of equipment (Holsen *et al*., 1991, Ajanaku *et al*., 2015). It becomes imperative to protect both the inner and outer surface of pipes used for industrial and domestic purposes. Electroplating, dip-coating and the use of natural inhibitors are some of the ways corrosion can be controlled. Inhibitors could be cathodic, anodic, mixed or volatile (Agarwal and Landolt, 1998; Ajanaku *et al*., 2014).

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Classification can also be based on inorganic, organic and green inhibitors. Green inhibitors (due to their sources) are found to be free from toxic materials, which inorganic and organic inhibitors are susceptible to (Singh *et al*., 2012). Recently, researchers have been conducting research works on different plant extract for corrosion control. This gear towards green inhibitors is in response to the fact that green inhibitors are inexpensive, biodegradable and highly available in our society (Labriti *et al*., 2012; Olusegun *et al*., 2013). Furthermore, greeninhibitors possess phytochemical constituents (such as tannins, steroids, terpenoids, saponins and alkaloids) that are responsive to its inhibitive attributes (Abdel-Gaber *et al*., 2008; Raja *et al*., 2008). Rosemary leaves were found to provide inhibitive tendencies on Al-Mg alloy corrosion in chloride solution (Kliskic *et al*., 2000). Inhibitive investigations have also been carried out on carbon steel in low chloride media using aqueous solution of *Hibiscus rosa-sinensis Linn* (Amuradha *et al*., 2008). Leaf extracts of *Dialumguineense*and *Euphorbia hirta* have also been used as inhibitive material on aluminium alloy in 0.5 MHCl solution (Anozie *et al*., 2011). This present study investigates the inhibitive traits of alcohol extract of *Jatrophacurcas*on the deterioration of zinc alloy in 1.50MHCl solution at a temperature of 28 ºC using gasometric method.

Jatrophacurcas is a plant that is easily propagated plant by stem and seed. It is often used to demarcate graves and boundaries of fields or farmlands. The stem and twigs are used in Nigeria and Cameroun as chew stick. The watery sap can be used to treat fresh cut and sores in some nations in Africa. The stem is used as support for leguminous crops in Gabon. The dried fruits are powdered and taken with food to void excessive fat by inducing diarrhea and vomiting. It also serves as medicine to ease stomach ache. The fruit and the seed are reported to contain a contraceptive principle (Burkil, 1994).

MATERIALS AND METHODS

Preparation of Zinc coupons

Zinc metal plate used was cut into coupons of 24 × 14 × 1mm thickness measurement using manual edge metal cutter. The coupons were carefully examined in order to prevent rough edges on the coupons from influencing corrosion. Surface treatment of the coupons was done by degreasing in absolute ethanol and drying in acetone. They were then stored in moisture free desiccators before use.

Optical emission spectrometer was used in analyzing the Zinc composition of the samples.

Table 1. Composition of the Zinc sample used for the study

Elements	Wt. %
Zn	99.4
Sn	<0.001
Sb	<0.001
Cd	0.018
Al	0.0014
Cu	0.0049
Pb	0.06
Fe	0.011

Extraction of *Jatrophacurcas* leaves

Leaves of *Jatrophacurcas,* were air dried and ground into powder. 100g of which was weighed into 1000ml of 90% methanol in a 2 liter volumetric flask. The flask was properly corked and left to stand for 48 hours with occasional shaking (Orubite-Okorosaye and Oforka, 2004). The resultant mixture was filtered and the methanol was evaporated to obtain thick slurry at 65°C using rotatory evaporator. 1.0 liter stock solution was prepared from the dark brown sticky extract obtained using 1.50 M Hydrochloric Acid solution in 1liter. Serial dilutions to various volume/volume (v/v) extract concentrations of 20%, 30%,40% and 50% solutions using 1.50MHCl solution.

Corrosion inhibition using Gasometric method

The gas-volumetric technique based on the evolution of gas from metal/corrodentinter-phase provides a fast experimental period and reliable results. Each of the specimens was dropped into the mylius cell containing 60 ml of the blank solution with concentration of 1.50 M HCl at 28 ºC and the volume of hydrogen (H_2) gas evolved per min interval was recorded.

A volume/volume (v/v) dilutions of 10%, 20%, 30%, 40%, 50% was utilized, to study the inhibitive effect and the volume of H_2 gas evolved per min interval was also recorded. At the end of each experiment of hydrogen evolution, the zinc specimen was withdrawn from the mylius tube and weighed, in likeness with method used by Eddy *et al*., (2010). A graph of volume against time interval was carried out. The inhibition efficiency (I.E.) was then determined using equation 1 (Oka for *et al*., 2005). The Inhibiting potential of the *Jatrophacurcas* leave extract can be ascertain by its Inhibition Efficiency and the degree at which it could be adsorbed on the Zinc metal surface. And this was calculated using:

$\%I.E. = \{1 - (V_{in}/V_{uni})\} \times 100$……………………..……..*equ*. 1

Where V_{in} = Volume of hydrogen evolved at time t for inhibited solution

V_{uni} = Volume of hydrogen evolved at time t for uninhibited solution

$\theta = \%I.E./100$…………………..…………………………*equ*. 2

Where θ = Surface coverage of the extract on the coupons

The hydrogen gas evolution and mass loss is produced by the same reaction

$Zn_{(solid)} + 2H^{+}_{(aqueous)} \rightarrow Zn^{2+}_{(solid)} + H_{2(gas)}$…………………*equ*. 3

The following relationships were obtained based on above equations and from the literatures.

$\Delta V \ \alpha \ \Delta W$...*equ*. 4.

$d\Delta V/dt \ \alpha \ d\Delta W/dt$

but

$R \ \alpha \ d\Delta W_m/dt \ \alpha \ d\Delta V_{H2}/dt$..*equ*. 5

Rate of corrosion R was modelled from H_2 gas evolved to the rate of material loss:

Where α = proportional sign
V_{H2} = Volume of Hydrogen Gas released (cm^3)
W_m = Metal weight loss due to chemical reaction (g)
R = Corrosion rate
t = time (minutes)

Correlating volume of hydrogen gas evolved with time of evolution by polynomial regression analysis using Statgraphics model. Ajayi *et al.* 2011:

$V_{in} = a \pm bt \pm ct^2$ ………………………………………..*equ*. 6
.
Where V_{in} is the volume of hydrogen gas evolved in the presence of inhibitor.

The Corrosion rate was calculated by differentiating the derived model:

$R = dV_{in}/dt = \pm b \pm ct$……………………………..…….*equ*. 7

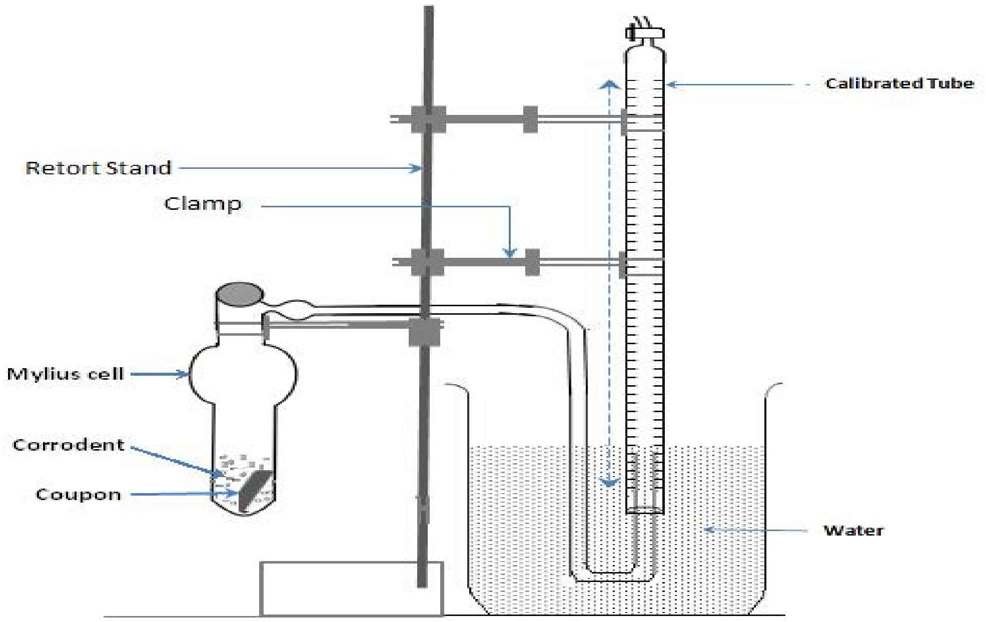

Figure 1. Experimental set up for Gasometric method

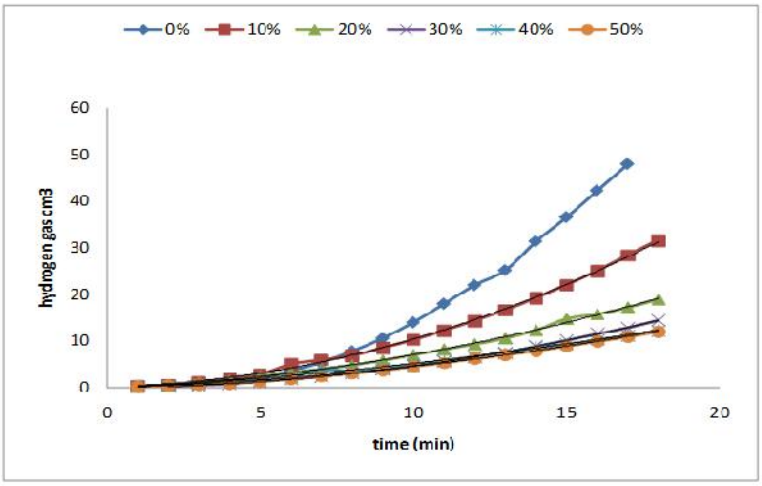

Figure 2. Relationship of Hydrogen gas evolved(cm^3) at different Time intervals (minutes) for Zinc corrosion in *Jatropha curcas* extracts in the presence of 1.50 MHCl at 28^{o}C

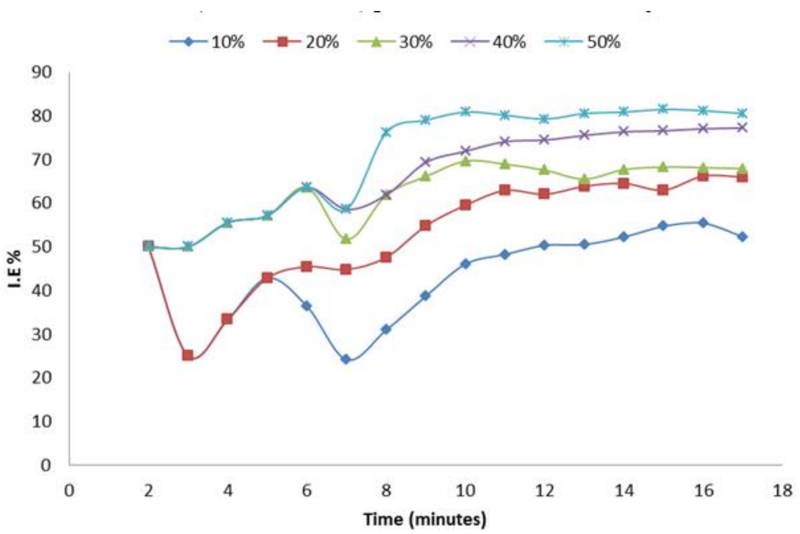

Figure 3. Plot of Inhibition Efficiency (.%) against Time (minutes) for Zinc corrosion in *Jatropha curcas* extracts in the presence of 1.50 MHCl at I.E (%) with Time (minutes)

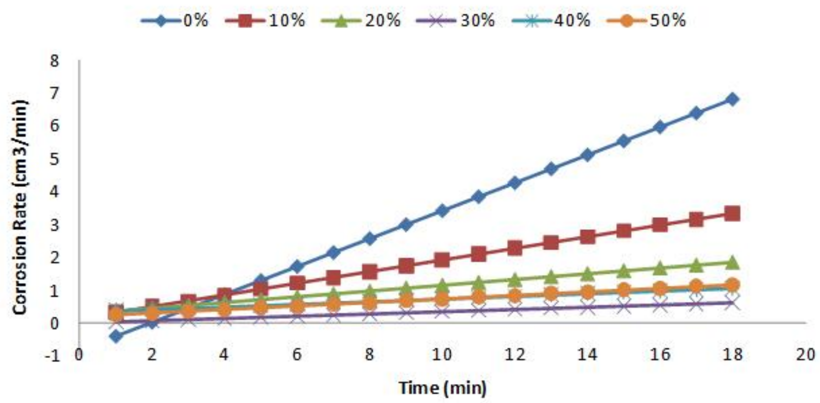

Figure 4. Corrosion rate (cm^3/minutes) of varying volume dilution ratios of extracts with time intervals (minutes) for Zinc corrosion in *Jatropha curcas* extracts in the presence of 1.50 MHCl at 28^{o}C

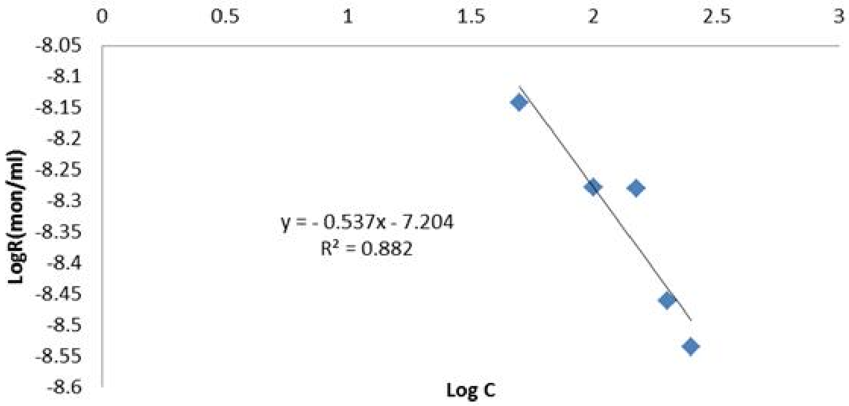

Figure 5. Plot of Corrosion rate log r (mol/min) against log of various *Jatropha curcas* leave extracts concentration C (mole) at 16th minutes for Zinc inhibition in the presence of 1.50 MHCl at 28^{o}C

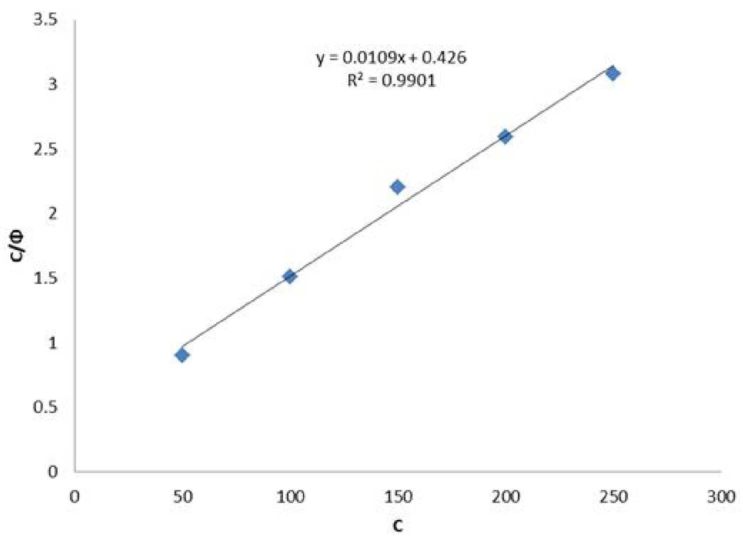

Figure 6. Plot of Concentration C of acid extracts against C/θ showing agreement with Langmuir isotherm for Zinc in *Jatropha curcas*leave extract

For measurement of zinc in *Jatrophacurcas* relating to 10% v/v ($50cm^3$ extract in make up to $500cm^3$) concentration, the corrosion rate model is shown as:

$$V = 0.0068t^2 + 0.003t - 0.0036$$

$$dV/dt = 0.0136t – 0.003$$

RESULTS AND DISCUSSION

Inhibition characteristics of *Jatrophacurcas* leave extract on zinc

The present investigation shows that Zinc metal is highly susceptible to acids attack; this is revealed as effervescence occurs within a minute of its existence in the 1.50 M HCl corrosion mylius cell set-up. The evolution of H_2 from the specimen increases with time.After which, the release of the gas subside due to the formation of inhibitor layer on the metal sample which now hinder the rate of corrosion.

Inhibitive efficiency of *Jatrophacurcas* on zinc metal

Figure3 showed increase inhibition efficiency with increase in time due to continuous adsorption of the leave extracts on the metal plates. 80% inhibitive efficiency was achieved at 50% extract concentration and the least (i.e. 10% dilution) gave20% Inhibition efficiency.

Corrosion rate of *Jatrophacurcas*

Corrosionrate as a function of extract concentration is revealed in Figure 4.

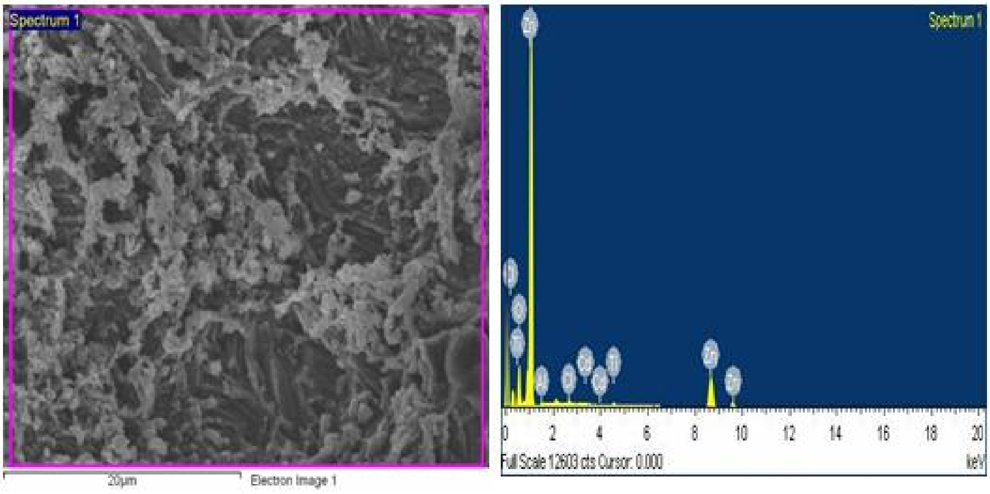

Figure 7.0 (a) SEM IMAGE of Corroded Zinc in 1.5MHCl(Control), (b) EDX Spectrum of Corroded Zinc in 1.5MHCl(Control)

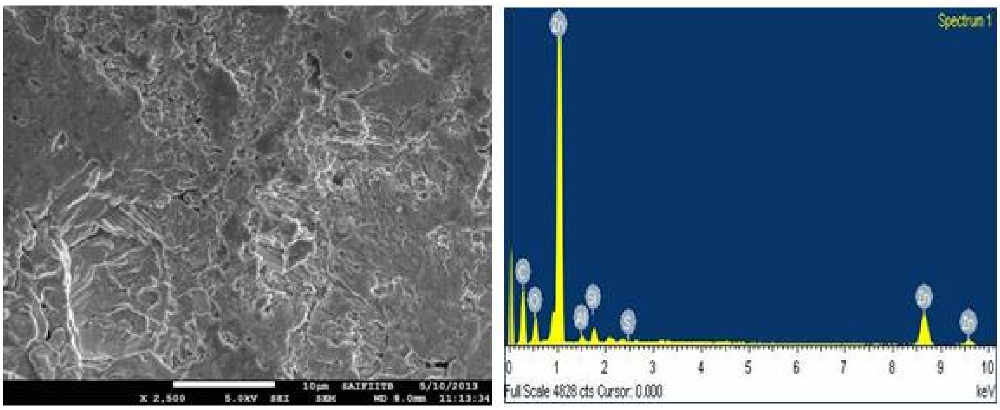

Figure 8.0 (a) SEM IMAGE of Zinc covered with*Jatropha curcas* extract (b) EDX Spectrum of protected Zinc in *Jatropha curcas* extract

Apart from protective surface layer of oxide and carbonate $[Zn_5(OH)_6(CO_3)_2]$ forms as the zinc corrodes. This protection lasts even after the zinc layer is scratched but degrades through time as the zinc corrodes away. The rate of hydrogen gas discharge is inversely proportional to the concentration of the extracts. This implies that as concentration of extracts increased the volume of hydrogen evolved decreased as observed in Figure 2. However, the 40% and 50% dilution shows marginal inhibitive differences.

Kinetics Relationship for Corrosion reaction

The concentration dependence of Corrosion rate can be expressed as indicated below,Mathur*et al*1982

$r = kC^B$

$\log r = \log k + B \log C$……………………………..………*equ* 8

Where: LogR(mol/min) =log of corrosion rate
k=Specific reaction rate constant (mol min^{-1}),

B=Reaction constant (mol^{-1}) (the negative value infer decreasing slope due to the inhibition of effect of the extract on the metal

$C_{extract}$=Extract Concentration in stock solution (mol).

Corrosion rates can therefore be related to extract concentration by conversion of volume of hydrogen gas evolved in the presence of inhibitor from units of ml (cm^3) to mol assuming hydrogen evolution took place at $1.01325x10^{-5}$Pa. (Ehteram *et al*., 2008). Also converting volume of extracts in ml (cm^3) to mole which have been variously employed in different studies (Ajayi *et al*., 2011; Mathur *et al*., 1982). Graph of relationship between logr and logC in Figure 5 gave linear expression from where k and B were obtained. The negativity of the slope obtained in this study indicates inhibitive action of the extract compared to that of (Ehteram *et al*., 2008) when no inhibitor was used.

Half-life of the Zinc in the extract

In Figure 5, it was observed that the slope decreases with decrease in reaction rate due to increase in concentration of extract. The larger the magnitude of the intercept, the greater the value of log k which is solution or reference level of logr at extrapolated zero concentration level of a particular extract. A higher intercept represent a higher starting rate of the reaction in a particular extract. Intercept = - 7.204

k = 6.251726928E08

Consequently Half Life ($t_{1/2}$) of the metal in the corrosive media: $t_{1/2}$=ln2/k ……………………………….…………….*equ* 9

Where $t_{1/2}$ is the half-life of the Zinc in acidic *Jatrophacurcas* extract and k is the Specific Reaction constant.

$t_{1/2}$=$0.110872913x10^8$minutes

Adsorption Isotherm

Adsorption is the mechanism by the extracts from plant origin made its phytoconstituents avaible for chemo-activities with the metal the adsorbate. The Surface coverage θ of adsorped plant extracts on the adsorbate at a given temperature give an insight into the theoretical studies of isotherms. Out of the four adsorption isotherms Temkin, Fruendlich, Frumkin and Langmuir studied, Langmuir is the most fitted isotherm with correlation coefficient (R^2) of 0.99 identical to physical adsorption

Table 2. Correlation Coefficient of Adsorption isotherms obtained from *Jatropha curcas* extract on Zinc at 16th minutes

Adsorption Isotherm	Correlation Coefficient (R^2)
Langmuir	0.990
Frumkin	0.925
Freundlich	0.376
Temkin	0.166

It is assumed to be of monolayer characteristics by the adsorbate for zero or one adsorbed molecule per site 0<θ<1, with all sites having the same adsorption energy and no interaction between adsorbed species or adsorption sites. It is represented by the equation:

C/θ = 1/k + C……………………………..…………………*equ* 9

(Lebrini *et al*., 2006)

Where Ø = Surface coverage; C = Concentration of extracts in acid solutions

k = characteristics constant related to adsorption intensity or degree of adsorption favourability

Graph of C/Ø (x-axis) against C (y-axis), was discovered to have a slope of 1 and intercept 1/k, from where k can be simply deduced.

Free energy of adsorption

For equation y =0.10x+0.426, 1/k= 0.426, Therefore characteristic constant k=2.3474.

ΔG = -kRT ΔG=-2.3474 x $8.314JK^{-1}mol^{-1}$ x 301K. The negative value of ΔG ($5,874.4014Jmol^{-1}$) depicts that the adsorption of extract on the zinc surface is a spontaneous process. $5.87KJmol^{-1}$ indicates physical adsorption

Surface morphological Analysis

The internal structure in Figure 7.0(a) was much attacked by acid in the absence of the leave extract. These have made much of α-Zinc phase to dissolve in to the acid solution. Leaving behind the exposed phases such Zn-Cd, Zn-Ti, Zn-Al. The surface of the zinc metal is covered with patches of corrosion products. Figure 7.0(b) indicates dominants of Zinc peak over the alloy constituents and corrosion products. In Figure 8.0(a) Protection was provided by inhibitory activities of phytoconsituent of *Jatrophacurcas leave* extract. The grains were much covered by adsorped extract. Less of prominent α-Zinc dissolve into the solution and other phases making up the alloy were protected from dissolving into acidified extract solution.

Conclusion

The Inhibition efficiency increased with increase in extract concentration as a result of increase in surface coverage of the extract on the metal. This was achieved by physisorption chemo-acitivities of the extract phytoconstituents on the metal surface.. Free energy of adsorption of - $5.87KJmol^{-1}$ indicated a spontaneous process of physical adsorptionof the extract on the zinc surface. Morphologically the adsorped film of the extract retarded dissolution of α-Zinc and other phases of the alloy into the corrodent, thereby protecting the internal grains of the metal. *Jatrophacurcas* leave extracts was confirmed from this investigation to be an effective inhibitor for Zinc metal in1.5 M HCl.

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