International Journal of Advanced Engineering and Technology
ISSN: 2456-7655; Impact Factor: RJIF 5.54
Received: 05-11-2018; Accepted: 09-12-2018
www.newengineeringjournal.com
Volume 3; Issue 1; January 2019; Page No. 01-09

Evaluation of plant extract as anti-corrosion for zinc in 1.0 m HCL. Using response surface methodology

Ezeugo JO[1], Ikebudu KO[2]
[1] Department of Chemical Engineering, Chukwuemeka Odumegwu Ojukwu University, Anambra State, Nigeria
[2] Department of Mechanical Engineering, Chukwuemeka Odumegwu Ojukwu University, Anambra State, Nigeria

Abstract
Optimization of inhibitive action of the ethanol extract of oil from Picralima nitida seed, towards acid corrosion of zinc is tested using weight loss, and thermometric methods. It was found that the extract acted as a good corrosion inhibitor for zinc corrosion in 1.0 M HCl solution. The inhibition action of the extract was discussed in view of Langmuir adsorption isotherm. It was revealed that the adsorption of the extract on zinc surface is governed by spontaneous process. The inhibition efficiency (IE) increases in line with corresponding increase in extract concentration. The temperature effect of the corrosion inhibition on the IE was studied. Revelation from the studies indicated that the presence of extract increases the activation energy of the corrosion reaction. Furthermore, from the calculated thermodynamic parameters, it was observed that the extract provides a good protection to zinc against pitting corrosion in chloride ion containing solutions. FT-IR analysis of picralima nitida seed extract on pure and corroded product showed a gradual shift of the corrosion mechanism as 3952.4cm^{-1} stretch bond of aliphatic and aromatic peak shifted to 3940.82cm^{-1}strong and broad O-H alcohol. In much same way,2829.14cm^{-1} C≡C stretch bond of aldehyde shifted to 2643.86cm^{-1}O-H,stretch bond of carboxylic acid at a strong and very broad intensity. An optimal inhibition efficiency IE (%) of 86.78 was obtained at optimum inhibitor concentration of 1.2gl^{-1}, optimum temperature and time of 313k and 8 hrs respectively.

Keywords: zinc, corrosion, inhibition, picralima nitida seed, inhibitor, optimiszation

1. Introduction
Corrosion is an electrochemical process that gradually returns metals such as zinc to its natural state in the environment. In other words, corrosion can be said to be destruction of material resulting from exposure and interaction with the environment. It is a major problem that requires immediate confrontation for safety, environment, and economic reasons [1]. Zinc consists of wide variety of alloys used since ancient times. Building industry frequently uses zinc alloys in roofing of house and other construction work because of its ductility and malleability. Therefore, zinc alloys are widely used in the production of many components and die-casting fittings in automobile and manufacturing and the mechanical industry, thanks to its super or super plasticity.

Zinc, in spite of the so called super plasticity is not spared by corrosion, especially after prolonged period of exposure in corrosive environment, such as HCl. For this reasons a lot of efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors is one of them [2]. The use of green inhibitors for the control of corrosion of zinc and alloys which are in contact with aggressive environment is an accepted and growing practice [3- 5]. Large numbers of organic compounds are being studied to investigate their corrosion inhibition potential. Revelation of these studies shows that organic compounds are not only expensive, but also toxic to living beings [6].

Plant extracts and organic species have therefore become important as an environmentally acceptable, readily available, and renewable source for a wide range of inhibitors [7, 12]. They are the rich sources of ingredients which have very high inhibition efficiency [6] and re hence termed "Green Inhibitors" [10]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful uses of naturally occurring substances to inhibit the corrosion of the metals in acidic and alkaline environment have been reported by some research groups [14] to mention but a few. Research efforts to find naturally organic substances or biodegradable organic materials to be used as effective corrosion inhibitors of a wide number of metals has been one of the key areas in this research work.

The aim of this study is to optimize the inhibitive properties of *Picralima nitida* seed (PNS) extract onto zinc in hydrochloric acid media using response surface methodology (RSM). Several studies have already been carried out and have remained focused on the *PNS* extract for their various pharmacological activities. Firstly, *Picralima nitida* plant is a tree that can reach a height of 35 meters, but is usually less. It is a commonly used herbal remedy in West Africa. All parts of the plant are bitter throughout its distribution area. The seeds, barks, roots and leaves have a reputation as a febrifuge and remedy for malaria as well as also being extensively used for pain relief and treatment of chest and stomach problems, pneumonia and intestinal worms [12]. A decoction of the seed is taken as a treatment for measles.

Presently, to the best of our knowledge no reported work in area of environment has been carried out on the corrosion inhibitive properties of the *PNS* extract. Therefore, the aim of this research is to undertake a thorough investigation towards that, in 0.5 M H_2SO_4 using the seed extract of picralima nitida. The study was done using thermometric method, Gravimetric method and FT-IR analysis. The effect

of temperature and concentration on the rate of corrosion were also studied, and some thermodynamic and kinetic parameters were calculated, too.
Application of central composite design (CCD) for optimization using statistical approaches such as RSM can be employed to maximize independent variable factors (inhibitor concentrations, temperature and time) affecting corrosion inhibition processes in order to secure optimal expected responses, such as weight loss, corrosion rate and inhibition efficiency [13, 15].

2. Experimental Methods

2.1 Materials

Gravimetric and thermometric tests were performed on 99.988% Zn, other components (wt%) were: Pb 0.003, Cd 0.003, Fe 0.002, Sn 0.001, Cu 0.00, Al 0.001. The sheet of zinc was cut into coupons (2.6 x 2.6 x 0.015cm), cleaned and polished with emery paper to expose shining polished surface. The coupons were degreased with acetone in order to remove any trace of oil and impurities and finally washed with double distilled water, dried in air and then stored in desiccators prior to use. The aggressive solution of 0.5 M HCl was made from analytical grade, hydrochloric acid and distilled water. *PNS* collected from Uke in Anambra, Nigeria, was sun-dried for three days. The dried seeds were ground to increase the surface area and stored in a closed container. For every of the extraction process, 30 grams of the ground *PNS* were measured and soaked in 100 ml of ethanol for 48 hours. At the end of the 48hrs, each plant mixture was filtered. The filtrate is the mixture of the plant extract and the ethanol. The extract obtained in ethanol solvent was concentrated, the solvent was distilled off and the extract evaporated to dryness. The plant extract was weighed and stored for the corrosion inhibition study.

2.2 Fourier transforms infrared (FT-IR) analysis of *Picralima nitida seed (pure)* extract and corrosion production

The zinc was immersed in the HCl medium in the presence of the *PNS* extract. At the end of the corrosion study, the corrosion products in the beakers were collected with aid of sample bottles [15]. SHIMADZU FT-IR spectrophotometer, model: IR affinity – 1, 5/NA 2137470136 SI) was used for the determination of the functional groups of the PNS extract (pure) and corrosion products. Comparative analysis of various FTIR produced peaks were carried out in order to determine the exact functional groups for the corrosion inhibition process.

2.3 Thermometric Method of the Corrosion Inhibition Study

The measurements were carried out using a thermostat set at 30^0C for the zinc in free and inhibited H_2SO_4. The temperatures of the system containing the zinc and the test solution were recorded regularly until a steady temperature value was evaluated using eqn. (1) [14, 15, 16].

$$RN = \frac{T_m - T_i}{t} \quad (1)$$

Where
T_m and T_i are the maximum and initial temperatures (^{0}C) respectively and t is the time in minutes elapsed to reach T_m.

The inhibitor efficiency was determined using eqn (2)

$$IE\% = 1 - \frac{RN\ add}{RN\ free} \times 100 \quad (2)$$

Where
RN_{free} and RN_{add} are the reaction numbers for the zinc dissolution in inhibitor free and inhibited corrosive medium respectively.

2.4 Gravimetric Method (weight loss).

The gravimetric method was carried out applying one factor at a time. Considering the said method, the weight loss method was carried out at different temperatures and with various concentrations of the *PNS* extract. Weighed zinc coupons were separately immersed in 250 ml open beakers containing 200ml of 1.0 M HCl. More so, zinc coupons were separately immersed in 150ml open beakers containing 200ml of 1.0 M HCl with various concentrations of the extract.
The variation of weight loss was monitored periodically at various temperatures in the absence and presence of various concentrations of the extracts. At the appropriate time, the coupons were taken out, immersed in acetone, scrubbed with a bristle brush under running water, dried and reweighed. The weight loss was calculated as the difference between the initial weight and the weight after the removal of the corrosion product. The experimental readings were recorded. The weight loss (Δw), corrosion rate (CR) and inhibition efficiency (IE) were determined using the eqn. (3), (4), and (5), respectively. The surface coverage was obtained using equation 5 [17].

$$\Delta w = W_i - W_f \quad (3)$$

$$CR = \frac{w_i - w_f}{At} \quad (4)$$

$$(IE\%) = \frac{w_0 - w_1}{w_0} \times 100 \quad (5)$$

$$\theta = \frac{w_0 - w_1}{w_0} \quad (6)$$

Where
w_i and w_f are the initial and final weight of zinc samples respectively, W_1 and W_0 are the weight loss values in presence and absence of inhibitor, respectively. A is the total area of the zinc sample and t is the immersion time.

2.5 Effect of temperature on the corrosion rate

Effect of temperature on the corrosion rate was described using Arrhenius equation

$$CR = A\ e^{-Ea/RT} \quad (7)$$

Where CR is the corrosion rate of the zinc, A is the pre-exponential factor, Ea is the activation energy, and sand R is the universal gas constant. eq. (7) can be linearized to form eq. (8).

$$In\ (CR) = In\ A - \left(Ea/R\right)\left(\frac{1}{T}\right) \quad (8)$$

Considering the corrosion rate of the zinc at T_1 and T_2 as Cr_1 and CR_2, then eq. (8) can be expressed by eq. (9) [18, 20].

$$In\left(\frac{CR_2}{CR_1}\right) = \left(\frac{Ea}{2.303R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (9)$$

Thermodynamic parameter for the adsorption process
The heat of adsorption Q_{ads} (kjmol^{-1}) was calculated using eq. (10) [21]

$$Qads = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - log\left(\frac{\theta_1}{1-\theta_1}\right) \times \frac{T_2\,T_1}{T_2 - T_1}\right] \quad (10)$$

Where
R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperature T_1 and T_2 respectively.

2.6 Consideration of the adsorption isotherm
The data obtained for the degree of surface coverage were used to test for the applicability of different adsorption isotherms (Langmuir, Frumkin, Temkin and Flory-Huggins isotherms).

i) Langmuir Isotherm
Langmuir isotherm can be expressed by eq (11) [22, 23]

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (11)$$

Where
C is the concentration of the inhibitor, K is the adsorption equilibrium constant and θ is the degree of surface coverage. In logarithmic form, eq. (11) can be expressed in eq. (12)

$$\log\frac{C}{\theta} = \log C - \log K \quad (12)$$

ii) Frumkin isotherm
Frumkin adsorption isotherm can be expressed according to eq. (13)

$$\log\left(Cc) * \left(\frac{\theta}{1-\theta}\right)\right) = 2.303 log K + 2\,\alpha\theta \quad (13)$$

Where
K is the adsorption –desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer.

iii) Temkin isotherm
Temkin isotherm can be expressed by eq. (14) [19]

$$\theta = \frac{2.303\log K}{2a} - \frac{2.303\log C}{2a} \quad (14)$$

Where
k is the adsorption equilibrium constant, a is the attractive parameter, θ is the degree of surface coverage, C is the concentration of the inhibitor

iv) Florry-Huggins Isotherm
The Flory-Huggins isotherm can be expressed by eq. (15) [24].

$$\log\left(\frac{\theta}{C}\right) = \log k + x\log(1-\theta) \quad (15)$$

Where
x is the size parameter and is a measure of the number of adsorbed water molecules. The free energy of adsorption (ΔG_{ads}) was calculated according to eq. (16) [19, 20].

$$\Delta G_{ads} = -2.303RT \log (55.5K) \quad (16)$$

Where
R is the gas constant. T is the temperature, K values obtain from the isotherms (Langmuir, Frumkin, Temkin and Flory-Huggins isotherm) were used to obtain the values of ΔGads according to eq. (16).

3. Results and Discussion
3.1 FTIR Spectrophotometer is a strong instrument that can be used to identify the type of bonding, especially functional group (s) present in organic compounds. Table.1. shows the FTIR spectrum of the ethanol extract of *PNS* extract. Initial absorption at 3952.4 to 3543.24cm^{-1} (associated hydroxyl) was overlapped by the strong stretching bond of O-H.
The peak at 3477.62 to 3261.46 cm^{-1} is attributed to medium and often broad stretch band of amines and amides, N-H. Wave band 3141.8cm^{-1} and 3053.02cm^{-1} are variable stretch of alkyl and aldehyde bond group, C-H. The absorption band at 2971.96cm^{-1} stands for strong and very broad stretch of carboxylic acid (free bond of alcohol). Wave band of 2751.94cm^{-1}, 2829.14cm^{-1} are two-peaked medium stretch bond of aldehyde, C≡C. The peak at 2404.54 cm^{-1} to 2030.12 cm^{-1} represent variable and sharp stretch bond of alkyne and nitrite, C=N. Wave band 1837.48cm^{-1}, 1658.65 cm^{-1} are strong representative of stretch bond of acids, esters, anhydrides and aldehydes, C=O. The absorption bands 1597.8 cm^{-1}, 1439.54 cm^{-1} are multiple sharp, medium peaks stretch of aromatic bond, C=C. This showed that *PNS* extract contains mixtures of compounds, that is, alkaloids, flavonoids, phenolics, phytates, terpenoids, tannins and steroids [25].

Table 1: Peak, intensity and assignment of FTIR analysis on the shifting mechanism of *Picralimnitida* seed (PNS) extracts and corrosion products of zinc in HCl

***Picralima nitida* seed (pure extract)**			***Picralima nitida* seed (corrosion product**		
Peak (cm^{-1})	**Intensity**	**Assignment**	**Peak (cm^{-1})**	**Intensity**	**Assignment**
3543.21	Strong and broad	Stretch bond of aliphatic and aromatic. O-H	3536.4	Strong and broad	O-H, alcohol
3261.45	Medium and often broad	N-H, stretch bond of amines and amides	3199.7	Medium and broad	N-H, stretch bond of amine and amide
3053.02	Variable	C-H stretch of alkyl and aldehyde groups	2914.06	Variable	C-H stretch bond of aryl or vinyl sp∧2
2971.96	Strong and very broad	Carboxylic acid	2705.62	Medium, strong and very broad	O-H, stretch of aldehyde and carboxylic acid

2751.94	Medium, two peaks	C≡C or stretch bond of aldehyde	2493.32	Strong and very broad	O-H, stretch bond of carboxylic acid
2458.58	Strong and very sharp	O-H, stretch bond of carboxylic acid	1902.74	Variable and sharp	C≡C, C≡N stretch bond alkyne and nitrite
2277.16	Sharp and variable	C=N, nitrite and alkyne	1783.08	Strong	C-O, stretch of ketone and aldehyde
2030.12	Variable and sharp	C≡C stretch bond of alkyne	1655.7	Variable	C=C bond of alkene
1659.56	Strong	C=O, stretch bond of acids, esters, anhydride and aldehydes	1501.3	Variable	C=C stretch bond of benzene ring
1439.54	Medium peaks pattern of peaks depending upon the substituted pattern.	C=C aromatic stretch bond	1350.76	Variable	C-H, bond stretch in plane within aliphatic and aromatic C=C-H, Ar-H, bend out of plane

3.2 Results of the Corrosion Inhibition as Determined by Thermometric Studies

The effect of concentration of seed extracts of *Picralima nitida* on the reaction number (RN) and the inhibition efficiency (IE) of zinc in the 1.0 M HCl medium is presented in table 2. It was revealed that increase in concentration of the inhibitor lowers the reaction number. This is in agreement with previous observation [10, 25, 26]. More so, the inhibition efficiency increases with increasing concentration of the inhibitor.

Table 2: Effect of the *Picralima nitida* seeds extracts on the IE (%) of zinc in 1.0 M HCl mediums

Inhibitor concentration (gL^{-1})	RN	IE (%)
0	0.1714	
0.2	0.0927	45.93
0.45	0.0726	57.62
0.7	0.0447	73.91
0.95	0.0429	74.96
1.2	0.0382	77.74

3.3 Measurements

Fig. 1 represents the relation between time and inhibition efficiency of zinc in 1.0 M HClat various concentration of *PNS* extract while table 2 represent experimental results of weight loss and corrosion rate using one factor at a time. Examination of Fig. 1 revealed that the loss of weight increases

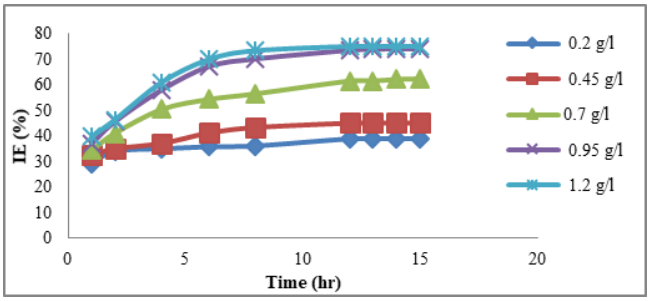


Fig 1: Represents the relation between time and inhibition efficiency of zinc in 1.0 M HCl at various concentration of *PNS* extract.

Linearly with increasing time in all tested solutions. However, the slopes of the obtained lines which represent the rate of weight loss are affected by addition of *Picralima nitida* extract. The presence of the extract causes a sharp decrease in the rate of weight loss. IEs at different concentrations of the extract were calculated using the equation:

$$IE(\%) = \frac{w_0 - w_1}{w_0} \times 100 \qquad (17)$$

Where w_1 and w_0 are the weight loss value in presence and absence of inhibitor, respectively.

3.4 Adsorption studies and inhibition mechanism

Table 3 revealed that the values of E_a and ΔG_{ads} indicated that the *seed* extract of PNS acted as a good corrosion inhibitor for the acid corrosion of zinc. The corrosion inhibition increases with increasing extract concentration. The gas chromatography-mass spectroscope analysis of the *PNS* extract revealed that the ethanol extract contains toluene, formula C_7H_8, molecular weight 92, cyclohexane having formula C_8H_{16}, molecular weight 112, hexane, 1,3-cyclopenta deine, molecular weight 156. It also contains at least ten non-volatile acids including eicosane and citric acids. The adsorption of the compounds on the electrode surface made barriers for mass and charge transfers [26]. The outcome of this situation leads to a protection of the metal surface from the attack of the aggressive anions of the acid. The extent of protection increases with increasing of the surface fraction occupied by the adsorbed molecules. As the extract concentration is increased, the number of the adsorbed molecules on the surface increases.

The results indicate that the adsorption of inhibitor molecules on the zinc surface follow Langmuir isotherm. In order words, the result suggests that there are no interactions or repulsion forces between the adsorbed molecules.

The standard adsorption free energy (ΔG_{ads}) was calculated using the following equation:

$$K = \frac{1}{999} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \qquad (18)$$

Where 999 is the concentration of water in solution expressed in gL^{-1}. R is gas constant, and T absolute temperature. The mean value of standard adsorption free energy (ΔG_{ads}) was 46.s4018 $kjmol^{-1}$. The negative values of ΔG_{ads} guarantee the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. It is generally known that, values of ΔG_{ads} up to -20 $KJmol^{-1}$ is consistent with electrostatic interaction between the charged molecules and the charged metal (physisorption). While those around – 40$kjmol^{-1}$ or higher are associated with chemisorptions as a result of sharing or transfer of electrons

from the molecules to the metal surface to form a coordinate type of bond [27]. Results of the present study, table 3, have shown various inhibition concentrations (gL^{-1}) and their respective activation energy (kj mol^{-1}). From the table, calculated Ea value for the inhibited solution with *PNS* extract is 40.45 and 46.89 $kjmol^{-1}$ in the presence of the inhibitor of 0.95 and 1.2 gL^{-1} extract concentrations, while with 0.45 and 0.70 gL^{-1} concentrations, activation energies are 34.38 and 18.65 $kjmol^{-1}$. The higher values of Ea suggest that dissolution of zinc in the presence of inhibitors is slow, indicating a strong inhibitive action of phytocompounds of alkaloids, flavonoids and tannins presence in *PNS* extracts, which leads to increasing the energy barrier for the corrosion process [29]. Actually, toluene molecules (the main compound of *PNS* extracts are easily protonated and exist in 0.5 M HCl medium in cationic form. Indeed, it is logical to assume that in this study, the electrostatic cat ion adsorption is responsible for the good protective properties of this compound.

Table 3: Activation Energy and Heat of Adsorption for the Corrosion Inhibitor of Zinc in 1.0 M HCl at various Inhibition Concentrations

Inhibitor concentration (gL^{-1})	Ea (kj mol^{-1})	$-\Delta G_{ads}$ (kj mol^{-1})
0.2	39.07	29.44
0.45	34.38	18.98
0.70	18.65	3.03
0.95	40.45	16.71
1.20	46.69	13.83

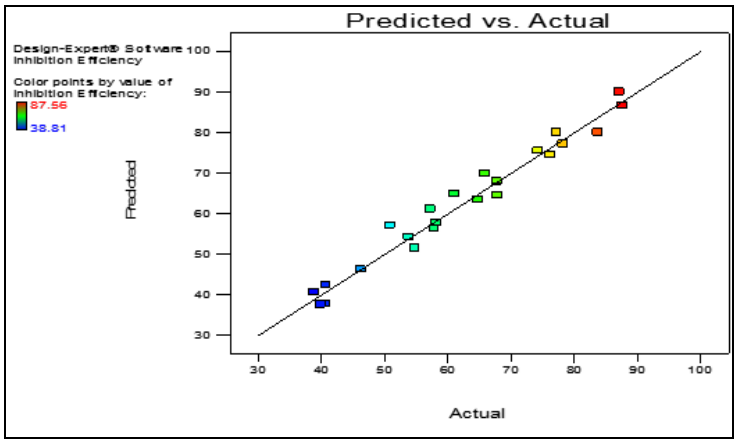
3.5 Results of the gravimetric method using RSM approach

The expected responses of weight loss, corrosion rate and inhibition efficiency to the independent variables, such as concentration, temperature and time in respect to corrosion inhibition of PNS extracts as a green corrosion inhibitor for zinc in HCl are listed in table 4.

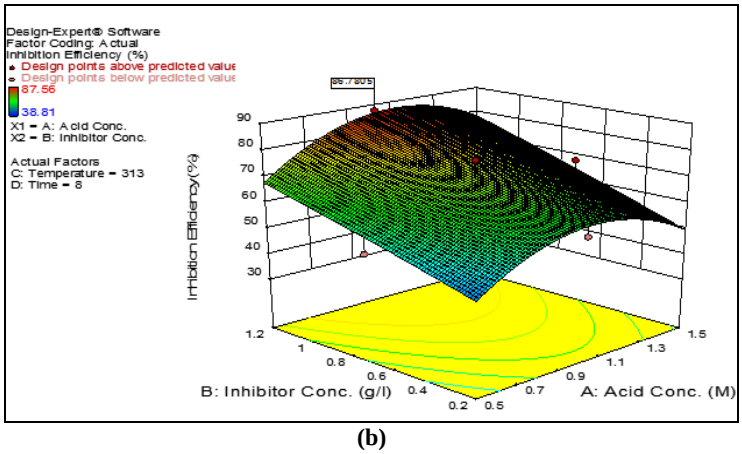
3.6 Graphical Analysis of the Inhibition Efficiency, IE (%), as determined using (RSM)

Response surface methodology (RSM) was used to analyze the response of corrosion inhibition of PNS extracts as a green corrosion inhibitor for zinc in hydrochloric acid solutions in figure 2. The ANOVA and graphical analyses of the corrosion inhibition efficiencies of PNS extracts for zinc in hydrochloric acid solutions were carried out. The equation 19 and 20 represent mathematical models in terms of coded and actual factors obtained. The model in terms of coded factors (inhibitor concentrations, temperature and time) was used to make predictions about the responses for given levels of weight loss, corrosion rates and inhibition efficiency of the studied corrosion processes. The high levels of the factors were coded as + 1 and the low levels of the factors were coded as -1. The optimum inhibition parameters obtained are presented in table…

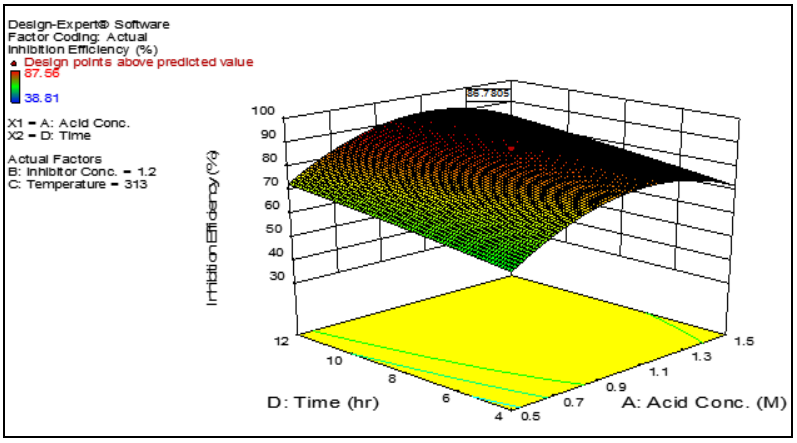
From the RSM graph predicted versus actual plot is used to testy the significance of the model's order. The predicted versus actual plot shows linear graph. The graphs (3-D surface plots) show the relationship between the factors and responses (inhibition efficiency, gravimetric and corrosion rate) of the designed experiment. Increase in concentration of the extract increases the inhibition efficiency of zinc in HCl solutions. Also inhibition efficiency reduces as temperature the system rises



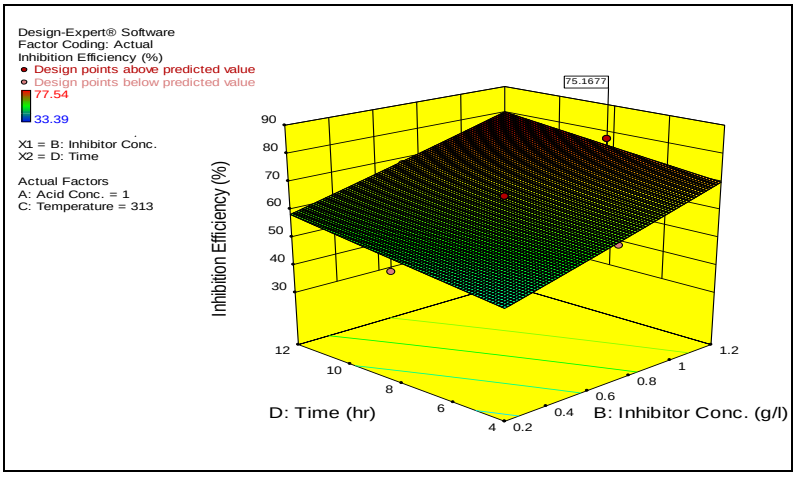
(a)



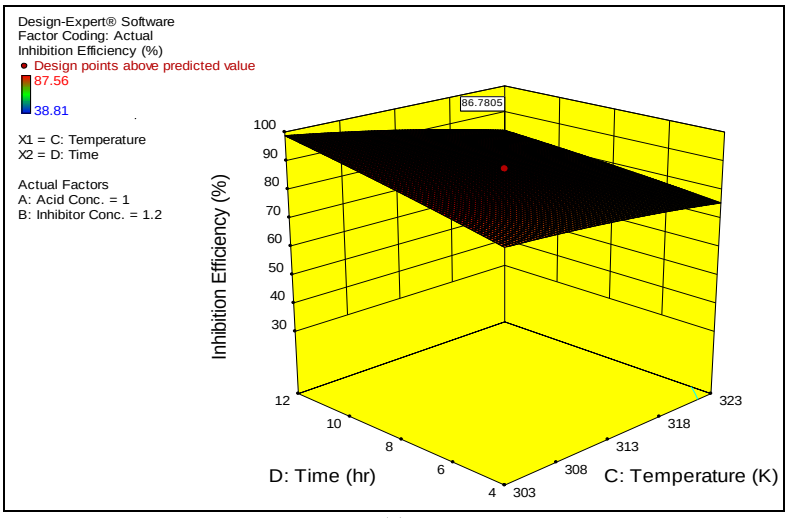
(b)



(c)



(d)



(e)

Fig 2: IE (%) of Zn in HCl Medium withPNS Extract Predicted versus actual IE (%) (b) IE (%) versus inhibition concentration and acid concentration (c) IE (%) versus time and acid concentration (d) IE (%) versus temperature and inhibitor concentration (e) IE (%) versus temperature and acid concentration.

3.7 Mathematical models of the inhibition efficiency of PNS extract on zinc in 0.1 M HCl

The equation 19 (coded factors) can be used to make predictions about the response for given levels of each factor (actual factors). By default, the high levels of the factors are coded as +1 and the low levels of the factors are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients

D30: ANOVA Response for inhibition efficiency of Zinc in HCl medium with *PNS* extracts. The Model F-value of 34.13 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, D, BC, CD, A^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required

to support hierarchy), model reduction may improve your model. The "Pred R-Squared" of 0.8326 is in reasonable agreement with the "Adj R-Squared" of 0.9412. The difference is less than 0.2."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 21.040 indicates an adequate signal. This model can be used to determine corrosion inhibition efficiency of PNS extract as a green corrosion inhibitor for zinc in HCl medium.

The final equations of corrosion of zinc immersed in acidic medium with PNS extract as inhibitor in terms of coded and actual factors are represented by eqns. (19) and (20):

Inhibition Efficiency PNS extract =+74.57+3.72* A+12.78* B-3.65* C+6.07* D+1.65* AB+0.49* AC+0.10* AD-2.10* BC-0.37* BD-2.01* CD-13.66* A^2-0.58* B^2-0.98* C^2-0.49* D^2…… (19)

Inhibition Efficiency of PNS extract =-1048.69305+81.18768* Acid Conc.+154.93148* Inhibitor Conc.+6.36152* Temperature+17.83458* Time+6.60750* Acid Conc. * Inhibitor Conc.+0.097375* Acid Conc. * Temperature+0.051563* Acid Conc. * Time-0.41937* Inhibitor Conc. * Temperature-0.18281* Inhibitor Conc. * Time-0.050328* Temperature * Time-54.63579* Acid $Conc.^2$-2.31579* Inhibitor $Conc.^2$-9.78947E-003* $Temperature^2$-0.030559* $Time^2$ …… (20)

Table 4: RSM Result of the Inhibition of Zn in HCl Medium with PNS Extract

Std	Run	Factor 1; A: Acid Conc. (M)	Factor 2; B: Inhibitor Conc. (g/l)	Factor 3; C: Temperature (K)	Factor 4; D: Time (hr)	Response 1, Weight Loss (g)	Response 2, Corrosion Rate (mg/cm^2hr)	Response 3, Inhibition Efficiency (%)
23	1	1	0.7	313	4	0.129	3.576	57.88
21	2	1	0.7	303	8	0.097	1.341	66.78
13	3	0.5	0.2	323	12	0.386	3.576	39.46
27	4	1	0.7	313	8	0.129	1.788	65.11
29	5	1	0.7	313	8	0.129	1.788	65.11
7	6	0.5	1.2	323	4	0.193	5.364	49.41
4	7	1.5	1.2	303	4	0.097	2.682	65.11
6	8	1.5	0.2	323	4	0.29	8.047	34.73
3	9	0.5	1.2	303	4	0.129	3.576	52.09
30	10	1	0.7	313	8	0.129	1.788	65.11
22	11	1	0.7	323	8	0.193	2.682	56.18
9	12	0.5	0.2	303	12	0.257	2.384	45.96
14	13	1.5	0.2	323	12	0.386	3.576	46.75
10	14	1.5	0.2	303	12	0.29	2.682	49.61
19	15	1	0.2	313	8	0.225	3.129	48.84
1	16	0.5	0.2	303	4	0.193	5.364	34.73
16	17	1.5	1.2	323	12	0.225	2.086	63.45
11	18	0.5	1.2	303	12	0.097	0.894	71.5
24	19	1	0.7	313	12	0.193	1.788	68.17
2	20	1.5	0.2	303	4	0.193	5.364	33.41
25	21	1	0.7	313	8	0.129	1.788	65.11
20	22	1	1.2	313	8	0.097	1.341	70.54
26	23	1	0.7	313	8	0.129	1.788	65.11
17	24	0.5	0.7	313	8	0.225	3.129	43.41
8	25	1.5	1.2	323	4	0.161	4.47	57.88
15	26	0.5	1.2	323	12	0.257	2.384	55.25
12	27	1.5	1.2	303	12	0.097	0.894	74.41
18	28	1.5	0.7	313	8	0.193	2.682	57.88
5	29	0.5	0.2	323	4	0.257	7.153	34.91
28	30	1	0.7	313	8	0.129	1.788	65.11

Table 5: ANOVA response for inhibition efficiency of Zinc in HCl medium with *Picralima nitida* seed extracts

ANOVA for Response Surface Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	4195.61	14	299.69	34.03	< 0.0001	Significant
A-Acid Conc.	177.41	1	177.41	20.15	0.0004	
B-Inhibitor Conc.	2031.82	1	2031.82	230.73	< 0.0001	
C-Temperature	171.62	1	171.62	19.49	0.0005	
D-Time	495.18	1	495.18	56.23	< 0.0001	
AB	33.52	1	33.52	3.81	0.0700	
AC	1.90	1	1.90	0.22	0.6486	
AD	0.27	1	0.27	0.030	0.8645	
BC	53.51	1	53.51	6.08	0.0263	
BD	0.94	1	0.94	0.11	0.7483	
CD	49.56	1	49.56	5.63	0.0315	
A^2	334.86	1	334.86	38.03	< 0.0001	

B^2	13.99	1	13.99	1.59	0.2268	
C^2	0.74	1	0.74	0.084	0.7762	
D^2	2.65	1	2.65	0.30	0.5913	
Residual	132.09	15	8.81			
Lack of Fit	132.09	10	13.21			
Pure Error	0.000	5	0.000			
Cor Total	4327.70	29				
Std. Dev.	2.97		R-Squared	0.9695		
Mean	55.63		Adj R-Squared	0.9410		
C.V.%	5.33		Pred R-Squared	0.8321		
PRESS	726.72		Adeq Precision	21.210		
-2 Log Likelihood	129.61		BIC	180.62		
			AICc	193.89		

Table 6: Optimum inhibition efficiency of Zn in 1.0 M HCl by PNS extract

Acid Conc.	Inhibitor Conc.(g/L)	Temperature (k)	Time (hr)	Optimum IE (%)
1	1.2	313	8	77.54

3.8 Validation of the results

To confirm the validity of the results, additional experimental were conducted. The chosen condition for the concentration, temperature and time are listed in tables (7), along with the predicted and measured inhibited efficiencies.

Inhibition efficiency was close to the predicted values which showed that RSM approach was appropriate for optimizing the corrosion inhibition process.

Table 7: Validation of optimal result for corrosion inhibition of Zn in 1.0 M HCl by plant extract

Acid Conc.	Inhibitor Conc. (g/L)	Temperature (k)	Time (hr)	Predicted IE (%)	Experimental IE (%)	Percentage error (%)
1	1.2	313	8	75.17	77.54	0.01

4. Conclusion

- The *Picralima nitida* seed extract acted as a good inhibitor for corrosion of zinc in 1.0 M solution. The IE increases with increasing extract concentration.
- The inhibitory action was carried out through adsorption of the extract compounds on zinc surface. The adsorption process is spontaneous, stable and obeys Langmuir adsorption isotherm.
- The adsorption process is physical as various studies techniques points towards physisorption. More so, the increase in temperature decreases the IE of the extract.
- The presence of *PNS* extract increases the activation energy of the corrosion reaction.
- The *PNS* extracts provide strong protection against corrosion of zinc in presence of chloride ions. The extent of protection increases with increasing extract concentration.
- PNS exhibit optimal inhibition efficiency IE (%) of 77.54, at optimal inhibition concentration of $1.2gl^{-1}$, temperature and time of 313k and 8 hrs respectively.

5. References

1. Abdel Rehim SS, Omar AH, Amin AM, Khaled FK. The corrosion inhibition of low carbon steel in concentrated sulphuric acid solutions. Part1: Chemical and electrochemical (AC & DC) studies. Corrosion Science. 2008; 50:2258-2271,
2. Abdel-Rehim SS, Khaled KF, Al-Mobarak NA. Corrosion Inhibition of Iron in Hydrochloric acid using pyrazole. Arabian Journal of Chemistry. 2011; 4:333-337.
3. Akalezi CO, Oguzie EE, Ogukwe CE, Ejele AE. Rothmannia Longiflora extract as corrosion inhibitor for mild steel in acidic media. Int. J Ind. Chem. 2015; 6:273-284.
4. Al-Otaibi MS, Al-Mayouf AM, Khan M, Mousa AA. Corrosion Inhibitory action of some plant extracts on the corrosion of mild steel in acidic media. Arabian Journal of Chemistry. 2014; 7:340-346.
5. Ameer MA, Fekry AM. Corrosion Inhibition of mild steel by natural product compound. Progress in Organic Coating. 2011; 71:343-349,
6. Aprael SY, Anees AK, Rafal KW. Apricot juice as green corrosion inhibitor of mild steel in phosphoric acid. Alexandria Engineering Journal. 2013; 52:129-135.
7. Ating EI, Umoren SA, Udousoro II, Ebenso EE, Udoh AP. Leaves extract of Ananas Sativum as green corrosion inhibitor for aluminium in hydrochloric acid solutions. Green Chemistry Letters & Reviews. 2010; 3:61-68.
8. Ayati NS, Khandandel S, Momeni M, Moayed MH, Davoodi A, Rahimizadeh M. Inhibitive effect of synthesized 2-(3-pyridyl)-3,4-dihydro-4-quinazolinone as a corrosion inhibitor for mild steel in hydrochloric acid. Material Scence & Physics. 2011; 126:873-879.
9. El-Etre AY. Inhibition of aluminium corrosion using Opuntia extract. Corrosion science. 2003; 45:2455-2495.
10. El-Etre AY. Inhibition of Aluminium corrosion using Opuntia extract. Corrosion Science. 2003; 45:2485-2495.

11. Fouda AS, Shalabi K, Idress AA. Ceratonia siliqua extract as a green corrosion inhibitor for copper and brass in nitric acid solutions. Green Chemistry Letters & Reviews. 2015; 8:3-4,17-29,
12. Gerengi H, Katarzyna S, Sahin HI. Corrosion-inhibiting effects of Mimosa extract on brass-MM55 corrosion in 0.5 M H_2SO_4 acidic media. J Ind. & Eng. Chem, 2012.
13. Ihebrodike MM, Nwandu MC, Okeoma KB, Nnanna LA, Chidiebere MA, Eze FC, *et al*. Experimental & theoretical assessment of the inhibiting action of Aspilia Africana extract on corrosion of aluminium alloy AA3003 in hydrochloric acid. J Materials Science. 2012; 47:2559-2572.
14. Khaled KF. Adsorption and inhibitive properties of a new synthesized guanidine derivative on corrosion of copper in 0.5M H_2SO_4. Applied Surface Science. 2008; 255:1811-1818,
15. Khaled KF. Corosion control of copper in nitric acid solutions using some amino acids – A combined experimental and theoretical study. Corrosion Science. 2010; 52:3225-3234,
16. Khaled KF. Studies of Iron corrosion Inhibition using Chemical, electrochemical & computer simulation techniques. Electro chemical Acta. 2010; 55:6523-6532,
17. Matjaz F, Jennifer J. Application of Corrosion Inhibitors for steels in acidic media for the oil and gas industry: A review. Corrosion Science. 2014; 86:17-41.
18. Migahed MA, Abdul-Raheim Atta AM, Brostow W. Synthesis & evaluation of a new water soluble corrosion inhibitor from recycled poly (ethylene terphethalate). Material Chemistry and Physics. 2010; 121:208-214.
19. Murthy ZVP, Vijayaragavan K. Mild steel corrosion inhibition by acid extract of leaves of Hibiscus Sabdariffa as a green corrosion inhibitor and sorption behavior. Green Chemistry Letters & Reviews. 2014; 7:209-219,
20. Narayana H, Praveen BM, Prasanna BM, Venkatesha TV, Abd Hamid SB. Anthranilic Acid as corrosion Inhibitor for mild steel in Hydrochloric Acid. Media. Procedia Material Science. 2014; 5:712-718.
21. Nnabuko OE, Momoh-Yaya H, Oguzie EE. Theoretical & experimental studies on the corrosion inhibition potentials of some Purines for aluminium in 0.1 M HCl. Journal of Advance Research. 2015; 6:203-217.
22. Oguzie EE. Evaluation of the Inhibitive effect of some plant extracts on the acid corrosion of mild steel. Corrosion Science. 2008; 50:2993-2998,
23. Oguzie EE, Iheabunike ZO, Oguzie KL, Ogukwe CE, Chidiebere MA, Enenebeaku CK, *et al*. Corrosion Inhibiting effect of Aframomum melegueta Extracts & Adsorption Characteristics of the active Constituents on Mild Steel in Acidic Media. Journal of Dispersion Science & Technology. 2013; 34:516-527.
24. Patchaiah K, Subbiah C, Seeni P, Gopalan S. Artemisia pallens as corrosion inhibitor for mild steel in HCL medium. Materials Chemistry & Physics. 2010; 120:643-648.
25. Quartarone G, Ronchin L, Vavasori A, Tortato C, Bonaldo L. Inhibitive action of gramine towards corrosion of mild steel in deaerated 1.0M hydrochloric acid solutions. Corrosion Science. 2012; 64:82-89.
26. Sanjay KS, Ackmez M, Gargi J, Essam K. Corrosion inhibition of Neem (Azadirachta indica) leaves extract as a green corrosion inhibitor for Zinc in H_2SO_4. Green Chemistry Letters & Reviews. 2009; 2:47-51.
27. Shaily BM, Alabbas FM, Rahul B, Spear JR, Brajendra M, Olson DL, *et al*. Neem extract as an inhibitor for biocorrosion influenced by sulfate reducing bacteria: A preliminary investigation. Engineering Failure Analysis. 2014; 36:92-103,
28. Thilagavathy P, Saratha R. Mirabilis Jalapa flowers extract as corrosion inhibitor for the mild steel corrosion in 1M HCL. Journal of Applied Chemistry. 2015; 8:30-35,
29. Torres VV, Amado RS, Faia de sa C, Fernandez TL, Carlos AS, Torres AG, *et al*. Inhibitory action of aqueous coffee ground extracts on the corrosion of carbon steel in HCl solution. Corrosion Sci. 2011; 53:2355-2392.
30. Umoren SA, Uduok UM, Israel AU, Obot IB, Solomon MM. Coconut coir dust extract: a novel eco-friendly corrosion inhibitor for AI in HCl solutions. Green Chemistry Letters & Rev. 2012; 5:303-313.
31. Zaabat RA, Makhloufi L, Alilat K, Maziz S, Saidani B. Effect of nettle plant extract on the cementation of copper onto zinc in acidic sulfate solutions. Hydrometallurgy. 2013; 136:58-64.
32. Zhang QB, Hua YX. Corrosion Inhibition of Mild steel by alkylimidazolium ionic liquids hydrochloric acid. Electrochemical Acta. 2009; 54:1881-1887,