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# Optimization of corrosion inhibition of *Picralima nitida* seed extracts as a green corrosion inhibitor for zinc in 0.5 M $H_2SO_4$

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**Abstract**
Optimization of inhibitive action of ethanol extract of *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 0.5 M $H_2SO_4$ solution. Further examination revealed that the adsorption of the extract on zinc surface is governed by spontaneous process. The inhibition efficiency increases as extract concentrations increases. Results of the FT-IR analysis of the seed extracts on pure and corroded product showed a gradual shift of the corrosion mechanism as 3971.7$cm^{-1}$ stretch bond of aliphatic and aromatic shifted to 3948.54$cm^{-1}$ strong and broad O-H alcohol. While 2798.26$cm^{-1}$ C≡C stretch bond of aldehyde shifted to 2416.12$cm^{-1}$ O-H, stretch bond of carboxylic acid at a strong and very broad intensity. Optimal inhibition efficiency, IE (%) of 77.54 was obtained at optimum inhibitor concentration of 1.2$gl^{-1}$, temperature and time of 313k and 8 hrs respectively.

**Keywords:** Zinc, corrosion, inhibition, *Picralima nitida* seed, inhibitor, optimization

## 1. Introduction
Corrosion is an electrochemical process that gradually returns metals such as zinc to its natural state sin 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 $H_2SO_4$. 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 synthetics 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- 11]. They are the rich sources of ingredients which have very high inhibition efficiency and hence termed "Green Inhibitors" [12]. 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 [13, 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 (Akuammidine)* seed extracts onto zinc in sulphuric 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 areas. The seeds, barks, roots and leaves have a reputation as a febrifuge and remedy for malaria.It is also used extensively for pain relief, treatment of chest and stomach problems, as well as pneumonia and intestinal worms [12]. The seed of *Picralima nitida* has chain preventive properties of flavonoids, phenolics, cardiac glycosides, steroids, tannins, saponins, terpenoids which attribute to their abilities to scavenge free radicals induce detoxification, inhibit stress response proteins and interfare with DNA binding activities of some transcription factor. Akuammidine has hypotensive, skeletal muscle relaxant and local analgesic activities. Its local analgesic activity is about three times as potent as cocaine. The powdered seed as a result of proven phytocompound are used in the treatment of pneumonia and other chest pains. They are also stimulants and tonic made from the seed have intensive bitter flavor. 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 extracts of picralima nitida. The study was done using thermometric and gravimetric method (one factor at a time). 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 ( inhibition 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 $H_2SO_4$ was made from analytical grade, sulphuric acid and distilled water. *PNS* collected from Uke in Anambra state, Nigeria, was sundried 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 each of the ground *PNS* were measured and soaked in 100ml 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 of *PNS* obtained in ethanol solvent was concentrated, distilled off the solvent and evaporated to dryness. The plant extracts was weighed and stored for the corrosion inhibition study.

### 2.2 Thermometric method of the corrosion inhibition study

The measurements were carried out using a thermostat set at $30^0$C 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) [14-16].

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

Where $T_m$ and $T_i$ are the maximum and initial temperatures (K) 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 number for the zinc dissolution in free and inhibited corrosive medium respectively.

### 2.4 Gravimetric Method

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 0.5 M $H_2SO_4$. More so, zinc coupons were separately immersed in 150ml open beakers containing 200ml of 0.5 M $H_2SO_4$ 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, 5), respectively. The surface coverage was obtained using equation 6 [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 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 eqn. (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 eqn. (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, $\theta_1$ and $\theta_2$ 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 eqn. (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)

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

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 eqn. (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 ($\Delta G_{ads}$) was calculated according to eqn. (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

### 3.2 Results of the Corrosion Inhibition as Determined by Thermometric Studies

The effect of concentration of PNS (inhibitor) extract on the reaction number (RN) and the inhibition efficiency (IE) of zinc in the 0.5 M $H_2SO_4$ medium is presented in table 1. The studies revealed that increase in concentration of the inhibitor lowers the reaction number. This is in agreement with previous observation [10]. More so, the inhibition efficiency increases with increasing concentration of the inhibitor.

**Table 1:** Effect of the *PNS* extracts on the IE (%) of zinc in 0.5 M $H_2SO_4$ medium

| Inhibitor concentration (gL$^{-1}$) | RN | IE (%) |
|---|---|---|
| 0 | 0.19 | |
| 0.2 | 0.11 | 44.35 |
| 0.45 | 0.84 | 55.19 |
| 0.7 | 0.06 | 69.58 |
| 0.95 | 0.05 | 74.40 |
| 1.2 | 0.04 | 76.81 |

### 3.3 Gravimetric Measurement

Fig. 1 represents the relation between time and inhibition efficiency of zinc in 0.5 M $H_2SO_4$ at various concentration of *Picralima nitida* seeds extract while table 2 represent experimental results of weight loss and corrosion rate using one factor at a time. Inspection of Fig. 2 reveals that the loss of weight increases.

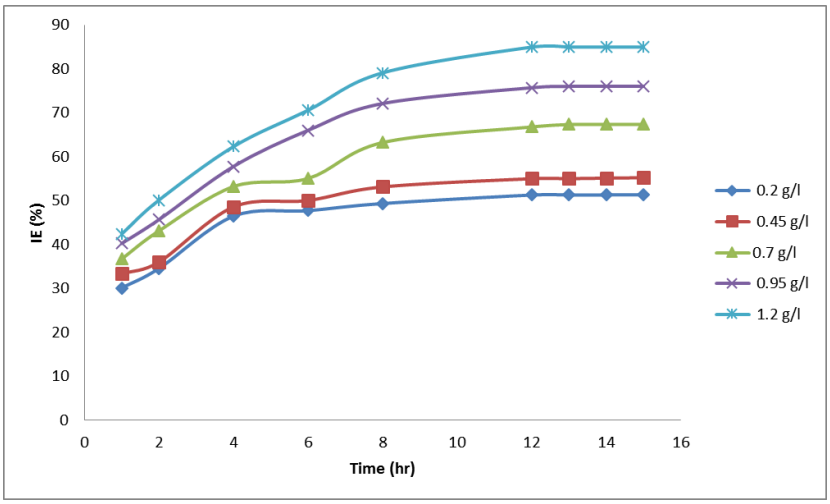



**Fig 1**

Fig. 2 represents the relation between time and inhibition efficiency of zinc in 0.5 M $H_2SO_4$ 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 *PNS* extract. The presence of the extract caused a sharp decrease in the rate of weight loss. Inhibition efficiencies at various concentration of the extract were calculated using equation (17).

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

Where $W_1$ and $W_0$ are the weight loss value in presence and absence of inhibitor, respectively.

Table 2, showed various inhibition concentration ($gL^{-1}$) and their respective activation energy (kj $mol^{-1}$). From the table, calculated Ea value for the inhibited solution with *PNS* extract is 52.404 and 82.985 $kjmol^{-1}$ 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 33.418 and 19.434 $kjmol^{-1}$. The higher values of Ea suggest that dissolution of zinc in the presence of inhibitor 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 [25, 28, 29]. Actually, toluene molecules (the main compound of *PNS* extracts are easily protonated and exist in 0.5 M $H_2SO_4$ 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 2:** Activation energy and heat of adsorption for the corrosion inhibitor of zinc in 0.5M $H_2SO_4$ at various inhibition concentrations.

| Inhibitor concentration ($gL^{-1}$) | Ea (kj $mol^{-1}$) | $-\Delta G_{ads}$ (kj $mol^{-1}$) |
|---|---|---|
| 0.2 | 11.81 | 13.01 |
| 0.45 | 3.47 | 2.19 |
| 0.70 | 4.59 | 2.39 |
| 0.95 | 37.09 | 23.02 |
| 1.20 | 39.31 | 23.9 |

### 3.4 Results of the gravimetric method using RSM approach

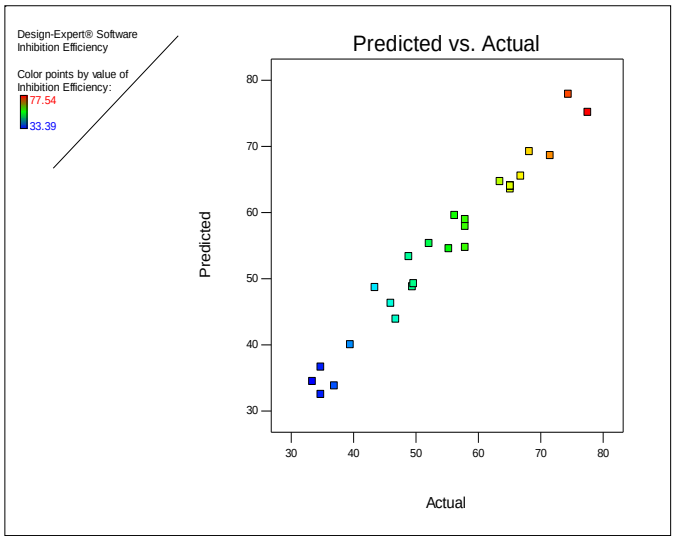
The expected responses of weight loss, corrosion rate and inhibition efficiency to the independent variables, such as concentration, temperature and time in respect to corrosion inhibition of picralima nitida leave extracts as a green corrosion inhibitor for zinc in $H_2SO_4$ are listed in table.

#### 3.4.1 Graphical analysis of inhibition efficiency, IE (%) of zn in $H_2SO_4$ medium with PNS extract as determined using (RSM)

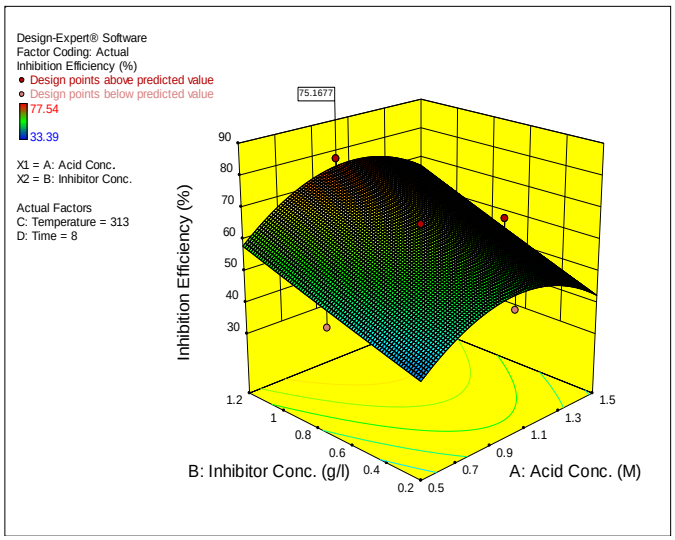
Response surface methodology (RSM) was used to analyze the response of corrosion inhibition of PNS extract as a green corrosion inhibitor for zinc in sulphuric acid solutions in fig. 2 (a-g). The analysis of variance, ANOVA and graphical analyses of the corrosion inhibition efficiencies of PNS extracts for zinc in sulphuric 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 concentration, temperature and time) was used to make predictions about the response 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 3.

From the RSM graph predicted versus actual plot is used to test the significance of the model's order. The predicted versus actual plot shows linear graph. The graphs of 3-D surface plots showed the relationship between the coded factors and responses (inhibition efficiency, weight loss and corrosion rate) of the designed experiment. Increase in concentration of the extract increases the inhibition efficiency of zinc in $H_2SO_4$ solutions. Also inhibition efficiency of PNS extract reduces as temperature of the system rises.

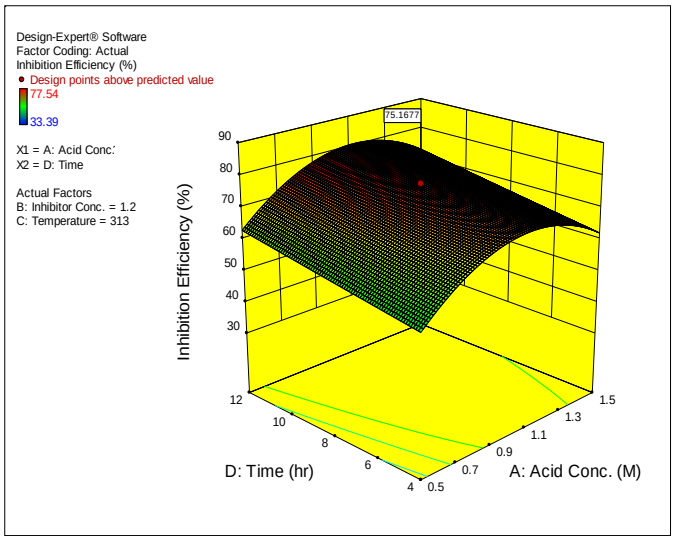
## Analysis of inhibition efficiency of Zn in $H_2SO_4$ Medium with PNS Extract




**(a)**




**(b)**

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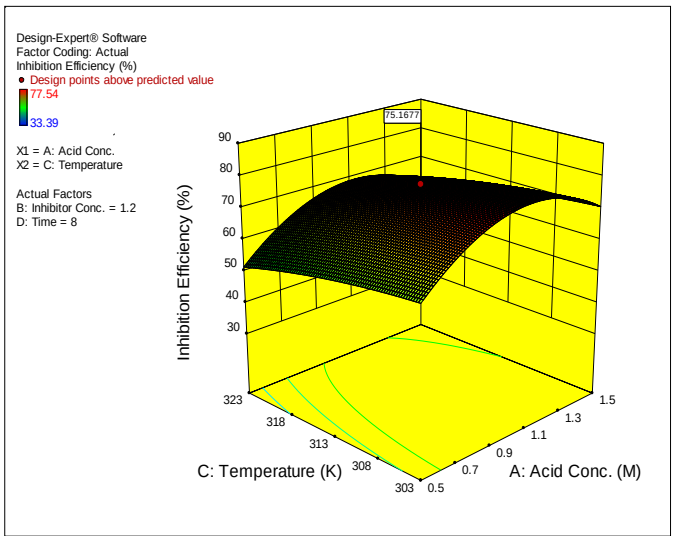
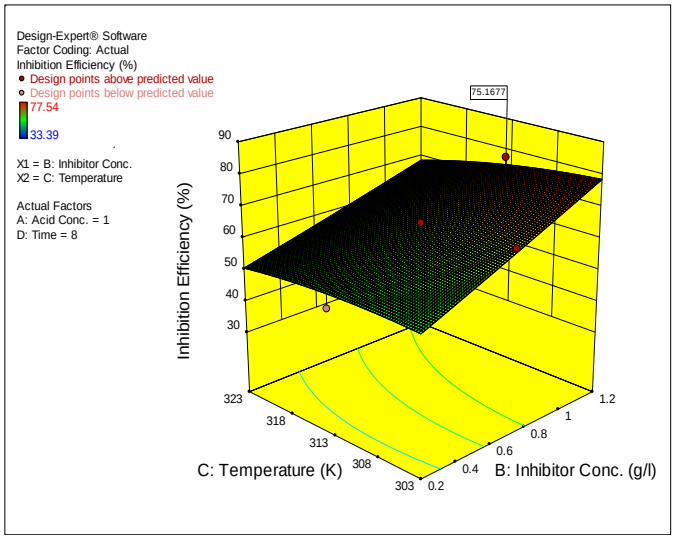
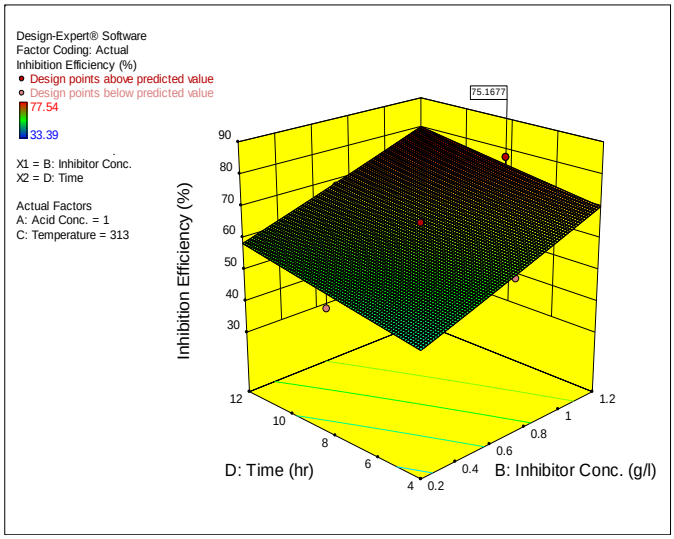


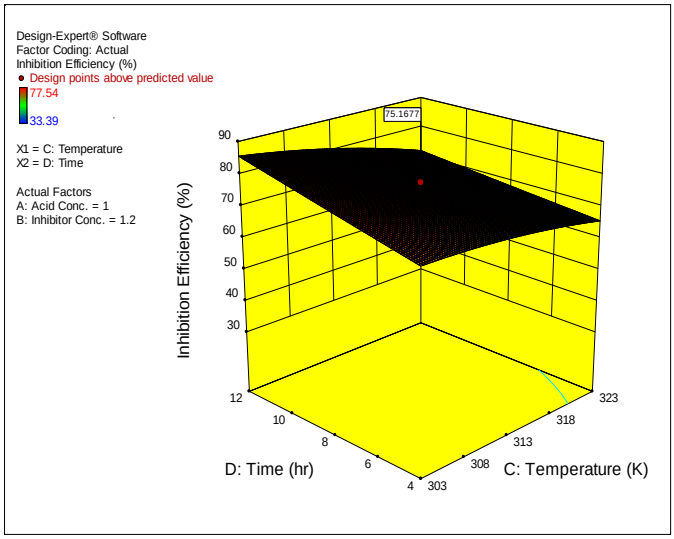

**(d)**




**(e)**




**(f)**




**(g)**

**Fig 2:** IE (%) of Zn in $H_2SO_4$ Medium with PNS 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 acid concentration (e) IE (%) versus temperature and inhibitor concentration (f) IE (%) versus time and inhibitor concentration (g) IE (%) versus time and temperature

### 3.4.2 Mathematical models of the inhibition efficiency

The equation 19 (coded factors) can be used to make predictions about the response for given levels of 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.

The Model F-value of 31.14 implies the model is significant. There is only 0.01% chance that an F-value this large could occur due to noise. Values of "Probe > 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 add values to the model. The "Pred R-Squared" of 0.8104 is in reasonable agreement with the "Adj R-Squared" of 0.9357; i.e. the difference is less than 0.2."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 20.302 indicated an adequate signal. This model can be used to navigate the design space of zinc in aggressive environment in absence and presence of PNS extract.

Final equations in terms of coded factors and actual factors are represented by eqns. (19) and (20) respectively.

Inhibition efficiency of PNS extract in terms of coded factors = +64.04+3.03* A+10.90* B-2.98* C+5.13* D+1.57* AB+0.22* AC+0.26* AD-1.95* BC-0.12* BD-1.89* CD-12.32* $A^2$+0.23* $B^2$-1.48* $C^2$+0.064* $D^2$ (19).

Inhibition efficiency of PNS extract in terms of actual factors = -1558.92747+85.30752* Acid Conc. +137.08854* Inhibitor Conc.+9.58163* Temperature+15.89395* Time+6.29500* Acid Conc. * Inhibitor Conc.+0.044250* Acid Conc. * Temperature+0. Inhibition efficiency of PNS extract in terms of coded factors 12750* Acid Conc. * Time-0.39100* Inhibitor Conc. * Temperature-0.059375* Inhibitor Conc. * Time-0.047156* Temperature * Time-49.26491* Acid Conc.$^2$+0.91509* Inhibitor Conc.$^2$-0.014812* Temperature$^2$+3.98575E-003* Time$^2$ (20).

**Table 3:** RSM result of the inhibition of Zn in $H_2SO_4$ 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$^2$hr) | Response 3, Inhibition Efficiency (%) |
|---|---|---|---|---|---|---|---|---|
| 23 | 1 | 1 | 0.7 | 313 | 4 | 0.182 | 5.066 | 57.88 |
| 21 | 2 | 1 | 0.7 | 303 | 8 | 0.137 | 1.9 | 66.78 |
| 13 | 3 | 0.5 | 0.2 | 323 | 12 | 0.547 | 5.066 | 39.46 |
| 27 | 4 | 1 | 0.7 | 313 | 8 | 0.182 | 2.533 | 65.11 |
| 29 | 5 | 1 | 0.7 | 313 | 8 | 0.182 | 2.533 | 65.11 |
| 7 | 6 | 0.5 | 1.2 | 323 | 4 | 0.274 | 7.6 | 49.41 |
| 4 | 7 | 1.5 | 1.2 | 303 | 4 | 0.137 | 3.8 | 65.11 |
| 6 | 8 | 1.5 | 0.2 | 323 | 4 | 0.41 | 11.4 | 34.73 |
| 3 | 9 | 0.5 | 1.2 | 303 | 4 | 0.182 | 5.066 | 52.09 |
| 30 | 10 | 1 | 0.7 | 313 | 8 | 0.182 | 2.533 | 65.11 |
| 22 | 11 | 1 | 0.7 | 323 | 8 | 0.274 | 3.8 | 56.18 |
| 9 | 12 | 0.5 | 0.2 | 303 | 12 | 0.365 | 3.378 | 45.96 |
| 14 | 13 | 1.5 | 0.2 | 323 | 12 | 0.547 | 5.066 | 46.75 |
| 10 | 14 | 1.5 | 0.2 | 303 | 12 | 0.41 | 3.8 | 49.61 |
| 19 | 15 | 1 | 0.2 | 313 | 8 | 0.319 | 4.433 | 48.84 |
| 1 | 16 | 0.5 | 0.2 | 303 | 4 | 0.274 | 7.6 | 34.73 |
| 16 | 17 | 1.5 | 1.2 | 323 | 12 | 0.319 | 2.955 | 63.45 |
| 11 | 18 | 0.5 | 1.2 | 303 | 12 | 0.137 | 1.267 | 71.5 |
| 24 | 19 | 1 | 0.7 | 313 | 12 | 0.274 | 2.533 | 68.17 |
| 2 | 20 | 1.5 | 0.2 | 303 | 4 | 0.274 | 7.6 | 33.39 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 25 | 21 | 1 | 0.7 | 313 | 8 | 0.182 | 2.533 | 65.11 |
| 20 | 22 | 1 | 1.2 | 313 | 8 | 0.137 | 1.9 | 77.54 |
| 26 | 23 | 1 | 0.7 | 313 | 8 | 0.182 | 2.533 | 65.11 |
| 17 | 24 | 0.5 | 0.7 | 313 | 8 | 0.319 | 4.433 | 43.41 |
| 8 | 25 | 1.5 | 1.2 | 323 | 4 | 0.228 | 6.333 | 57.88 |
| 15 | 26 | 0.5 | 1.2 | 323 | 12 | 0.365 | 3.378 | 55.25 |
| 12 | 27 | 1.5 | 1.2 | 303 | 12 | 0.137 | 1.267 | 74.41 |
| 18 | 28 | 1.5 | 0.7 | 313 | 8 | 0.274 | 3.8 | 57.88 |
| 5 | 29 | 0.5 | 0.2 | 323 | 4 | 0.365 | 10.13 | 36.91 |
| 28 | 30 | 1 | 0.7 | 313 | 8 | 0.182 | 2.533 | 65.11 |

**Table 4:** ANOVA Response for inhibition efficiency of Zinc in $H_2SO_4$ medium with *Picralima nitida* seed extract

| **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 | 4354.87 | 14 311.06 | 31.14 | < 0.0001 | Significant |
| A-Acid Conc. | 164.95 | 1 164.95 | 16.51 | 0.0010 | |
| B-Inhibitor Conc. | 2139.89 | 1 2139.89 | 214.23 | < 0.0001 | |
| C-Temperature | 159.37 | 1 159.37 | 15.95 | 0.0012 | |
| D-Time | 474.63 | 1 474.63 | 47.52 | < 0.0001 | |
| AB | 39.63 | 1 39.63 | 3.97 | 0.0649 | |
| AC | 0.78 | 1 0.78 | 0.078 | 0.7833 | |
| AD | 1.04 | 1 1.04 | 0.10 | 0.7514 | |
| BC | 61.15 | 1 61.15 | 6.12 | 0.0258 | |
| BD | 0.23 | 1 0.23 | 0.023 | 0.8825 | |
| CD | 56.93 | 1 56.93 | 5.70 | 0.0306 | |
| $A^2$ | 393.01 | 1 393.01 | 39.34 | < 0.0001 | |
| $B^2$ | 0.14 | 1 0.14 | 0.014 | 0.9088 | |
| $C^2$ | 5.68 | 1 5.68 | 0.57 | 0.4623 | |
| $D^2$ | 0.011 | 1 0.011 | 1.055E-003 | 0.9745 | |
| Residual | 149.83 | 15 9.99 | | | |
| Lack of Fit | 149.83 | 10 14.98 | | | |
| Pure Error | 0.000 | 5 0.000 | | | |
| Cor Total | 4504.70 | 29 | | | |
| Std. Dev. | 3.16 | R-Squared | 0.9667 | | |
| Mean | 55.93 | Adj R-Squared | 0.9357 | | |
| C.V. % | 5.65 | Pred R-Squared | 0.8104 | | |
| PRESS | 854.17 | Adeq Precision | 20.302 | | |
| -2 Log Likelihood | 133.39 | BIC | 184.40 | | |
| | | AICc | 197.67 | | |

**Table 5:** Optimum inhibition efficiency of Zn in $H_2SO_4$ by PNS extract

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

### 3.5 Validation of the results

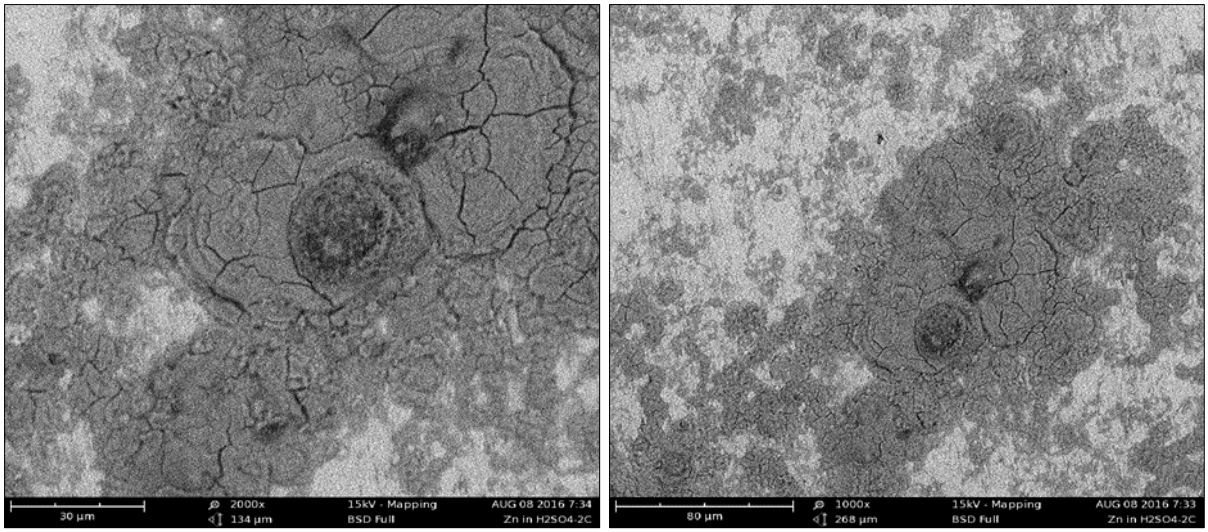
To confirm the validity of the results, additional experimental were conducted. The chosen condition for the concentrations, temperature and time are listed in tables (3), along with the predicted and measured inhibited efficiencies. Inhibition efficiency was close to the predicted values which showed that RSM approach was appropriate for optimizing the corrosion inhibition process. Similar result was reported by [30, 31]

**Table 6:** Validation of optimal result for corrosion inhibition of Zn in $H_2SO_4$ by PNS 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 | 0.03 |

### Morphological Examination

Fig. (a) Show the SEM image of zinc coupon immersed in solution of 0.5 M $H_2SO_4$ for 12hrs. The SEM image revealed that the surface was badly corroded as a result of aggressive attack by the sulphuric acid. Figure (b) showed SEM image of the zinc specimens immersed for the same period of time interval in 0.5M $H_2SO_4$ solution containing 1.2 $gL^{-1}$ of PNS extract. These images show that the adsorbed inhibitor film present on the zinc surface mitigated the dissolution of the base metal with high degree of efficiency (77.54%). It is also observed that there is significant morphological variation between the protective barrier formed on the zinc surface at 1.2$gL^{-1}$ of the extract and the one immersed in the solution free inhibitor. This observation is in clear agreement with the findings of [33-35].




**a** **b**

**Fig 3:** Morphological images obtained by optical microscope for (a) Zinc immersed in $H_2SO_4$ in absence of PNS extract (b) Zinc immersed in $H_2SO_4$ in presence of PNS extract as inhibitor.

## 4. Conclusion

1. The *PNS* extracts acts as a good inhibitor for corrosion of zinc sin 0.5 M $H_2SO_4$ solution. The IE increases with increasing extract concentration.
2. The inhibitory action was carried out through adsorption of the extract compounds on zinc surface prompting gradual decrease on the reaction number as the concentration of the PNS extract increases
3. The adsorption process is physical as various studies techniques points towards physisorption. More so, the increase in temperature decreases the IE of the extract.
4. The presence of *PNS* extract increases the activation energy of the corrosion reaction and Subsequently provides strong protection against corrosion of zinc in presence of sulphate ions. The extent of protection increases with increasing extract concentration.
5. PNS extract exhibit optimal inhibition efficiency, IE (77.54%), at optimal inhibition concentration of $1.2gl^{-1}$, temperature and time of 313k and 8 hrs respectively.

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