Modelling and Optimization Mechanism of *Bougainvillea glabra* Flower Extracton Zinc in 2 M Aqueous HCl using Response Surface Methodology

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***Abstract*:- Modeling and Optimization mechanism of flower extract of *Bougainvillea glabra* (GBF) on inhibition of zinc corrosion in 2 M aqueous HCL was studied using weight loss and Response surface methodology (RSM). The effects of temperature (303 -343K), time (2–10 hr), acid concentration (1.0 – 3.0 mols), and inhibitor concentration (0.2 – 1.0g/l) on inhibition efficiency was carried out using Response Surface Methodology. The rate of corrosion of zinc in aqueous acid solution was successfully hindered by BFE. The predicted values was validated by applying the optimum settings of 0.025g/l inhibitor concentration, time of 6.250 hr and temperature of 313K. The predicted model was quiet in agreement with the obtained experimental data of 87.23%. The activities of BFE as readily available, low cost and as good corrosioe n inhibitor of zinc in acid media was shown is this study.**

***Keywords*:- Acid corrosion, *Bougainvillea glabra* flower extract, modelling, inhibition efficiency, Response Surface Methodology.**

I. INTRODUCTION

Zinc is a metal with numerous industrial applications and is mainly used for the corrosion protection of steel. It is one of the most important non-ferrous metals, which finds extensive use in metallic coatings. Zinc and zinc-coated products corrode rapidly in moist atmospheres forming white corrosion product (white rust). Zinc is most commonly used for cathodic protection of metals. Since zinc has a sufficiently negative standard electrode potential, it is highly reactive and acts as sacrificial anode in cathodic protection[1-3]. Despite its highly negative electrode potential, a protective layer, either as zinc oxide or zinc hydroxide, forms on the metal surface in near- neutral aqueous solutions under normal atmosphere conditions which prevents its further reaction. This layer provides a better corrosion resistance for zinc, thus zinc is used as a galvanizing element for iron and steel.

Bougainvillea glabra is an evergreen, climbing shrub with thick, thorny stems and drooping branches that are glabrous or sparsely hairy. It is sometimes referred to as "paper flower" because the bracts are thin and papery. Tiny white flowers usually appear in clusters surrounded by colorful papery bracts, hence the name paper flower. The leaves are dark green, variable in shape, and up to 10 cm long. The flowers are about 0.4 cm in diameter (the pink petal-like structures are not petals, but bracts). *Bougainvillea glabra* can be used in treatment of several diseases for instance the infusion of the plant's tender leaves and bracts is used orally to treat gastrointestinal problems (diarrhoea, stomach pain), respirato conditions (asthma, bronchitis, catarrh, chestpain, fever, pneumonia, whooping cough) [4].

In the light of the above, the abundance of numerous phytochemical components (saponins, tannins, flavonoids etc) present in the extract x-rayed the importance of Bougainvillea glabra flower (BGFE) extract in the treatment of some ailments or diseases.

Hence, the aim of this assessment is to measure the enhancement of corrosion resistance of zinc by BGFE in 2 M HCl using weight loss approach and RSM analyses to elucidate its inhibition mechanism. Finally, the central composite design (CCD) was used to evaluate the consistence and significance of the process variables.

II. MATERIALS AND METHODS

2.1 Materials

The *Bougainvillea glabra* flower was collected from Agulu town and identified at the Department of Botany, Nnamdi Azikiwe University in Awka, Anambra State, Nigeria. Soxhlet extractor apparatus, HANNA pH meter model (pH – 211), memert (oven), Electronic analytical balance (JA303P) with sensitivity of ± 0.001g, and beakers, were employed for this corrosion study. Analytical grade chemicals were used throughout the study. The composition of zinc used was previously describe in [3].

2.1.1 Methods

a. Pre-treatment of sample

The *Bougainvillea glabra* flower was dried in an oven at 60°C for a period of 10 hours, ground to particle size of 500 µm and kept in desiccator for use.

b. Phytochemical analysis of Bougainvillea glabra flower

Analysis of Phytochemical components of *Bougainvillea glabra* flower extract was done to ascertain the major constituents in the extract. The methods of [5-9] were used for qualitative and quantitative analysis.

c. Extraction of Bougainvillea glabra flower extract:

1000 g of grounded *Bougainvillea glabra* flower sample was poured into U- shape thimble. This was then placed inside the 500 ml soxhlet extractor. 250 ml of ethanol was poured into a three - neck round bottom flask fixed to the extractor and the condenser was tightly secured at the top end of the extractor. This set up was heated on a jacketed heating mantle at 78°C for 8hrs.

2.2 Experimental procedure:

The corrosion inhibition study of zinc on BGFE was performed using the methods described before in [3,10]. The zinc coupon having dimension of 5 cm × 3 cm × 0.18 cm were polished with different sizes coarse (emery) paper, degreased with ether of petroleum and rinsed with distilled water and dried. The zinc coupon was suspended with the help of a thread in 150 ml beaker containing 100 ml of 2 M HCl with varying concentrations of the inhibitor. At time interval of 1 hour, 0.2, 0.4, 0.6, 0.8 and 1.0 g/l of inhibitor concentrations of 2 M HCl solution, and at various temperatures were studied. Individually the coupons was introduced in distilled water and immersed in methanol solution, scrubbed to eliminate residual acids and concentration of inhibitors then thoroughly washed with washing liquor before rinsing with distilled water and drying inacetone and finally reweighed. Tables 1 and 2 gives the experimental plan as recorded with design expert software.

2.2.1 Determination of Efficiency of inhibitor:

The corrosion inhibition efficiency was obtained from Equation (1);

$$\eta\% = \frac{W_0 - W_1}{W_0} \qquad (1)$$

2.3 Experimental design using RSM:

The Design Expert Software 10.0.3 as described previously in [10] was used to analyze the experimental. Central – Composite Design (CCD) of 30 experimental runs including 4- operating variables was recognized for the experiments used in studying the effects of acid concentration, inhibition concentration, time and temperature, on corrosion process parameters was carried out on the BGFE. The Factor levels with the corresponding real values are shown in Table 1. The matrix for the four variables was varied at 5 levels (-1, +1, 0, -1 and +1)

Table 1: Central-Composite Design factor levels of independent variables

Independent variables	-α	+1	0	+1	-α
Acid concentration (mols)	1.0	1.5	2.0	2.5	3.0
Inhibitor concentration (g/l)	0.2	0.4	0.6	0.8	1.0
Exposure time (Hr)	2	4	6	8	10
Temperature K	303	313	323	333	343

2.4 Optimization of the RSM Regression Model:

A regression model that describes the correlation between the percentage inhibition efficiency and the process factors was developed and state as:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{11} X^2{}_{11} + \beta_{22} X^2{}_{22} + \beta_{33} X^2{}_{33} + \beta_{44} X^2{}_{44} \qquad (2)$$

where Y is the response or dependent variable; X_1, X_2 $X_3$and $X_4$are the independent variables; β_0,β_1,β_2,β_{11},β_{22},β_{12} etc are the regression coefficients [10,11]..

III. RESULTS AND DISCUSSION

3.1 Modelling of inhibition efficiency and Analysis of statistical

Analysis of variance (ANOVA), regression analysis and the response of the surface plots was obtained by using Design Expert 10.0.1 version software to analyze the experimental data. The weight loss, corrosion rate, inhibition efficiency and Central composite design (CCD) results are presented in Table 2. The ANOVA result on Table 3 showed R^2 value of 0.9830 and Adjusted R^2 of 0.9671 correspondingly. The variance of ± 0.2 in the values of Predicted R-squared and Adjusted R-squared indicates close agreement between the two as previous descried in (WSN). This implies that the experimental values was consistent and statistically significance hence a quadratic equation was appropriate for the model. The quadratic equation in final equation terms of the coded values of the process parameters.

Regression model for corrosion inhibition of zinc in HCl by *BGFE is*;

$$IE = -58.64+330.41A-12734.41B+51.22C+0.20D-3.42A*C-0.91A*D+67.64B*C+39.25B*D-0.15C*D-4.19A^2 \qquad (3)$$

Where;

A is acid concentration, B is inhibitor concentration, while C is time and D is temperature.

Table 2. RSM result of the corrosion inhibition of zinc in Hcl by *Bougainvillea glabra* flower extract (BGFE).

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2	Response 3
Std	Run	Acid conc	Inhibitor conc	Time	:Temperature	Weight loss	Corrosion rate	Inhibitor efficiency
		(mol)	(g/l)	(hrs)	(K)	(g)	(g/cm^2hr)	(%)
22	1	1.5	0.04	8	323	0.107	1.783	60.37
27	2	1.5	0.04	4.5	323	0.107	1.783	50.37
18	3	2.5	0.04	4.5	323	0.043	2.15	69.29
15	4	1	0.055	6.25	333	0.08	1.333	70.37
1	5	1	0.025	2.75	313	0.107	1.783	60.37
6	6	2	0.025	6.25	313	0.11	1.1	62.29
3	7	1	0.055	2.75	313	0.107	1.783	64.37
25	8	1.5	0.04	4.5	323	0.08	4	49.71
24	9	1.5	0.04	4.5	343	0.27	2.7	49.21
23	10	1.5	0.04	4.5	303	0.123	2.05	49
7	11	1	0.055	6.25	313	0.127	1.27	60.47
13	12	1	0.025	6.25	333	0.22	2.2	37.54
14	13	2	0.025	6.25	333	0.107	1.783	63.37
5	14	1	0.025	6.25	313	0.117	5.85	40.22
26	15	1.5	0.04	4.5	323	0.18	3	53.33
8	16	2	0.055	6.25	313	0.09	4.5	52.71
19	17	1.5	0.01	4.5	323	0.107	1.783	56.37
16	18	2	0.055	6.25	333	0.057	0.57	72.59
4	19	2	0.055	2.75	313	0.067	3.35	48.9
11	20	1	0.055	2.75	333	0.07	1.167	63.08
30	21	1.5	0.04	4.5	323	0.107	1.783	50.37
17	22	0.5	0.04	4.5	323	0.107	1.783	60.37
2	23	2	0.025	2.75	313	0.043	2.15	79.29
28	24	1.5	0.04	4.5	323	0.08	1.333	50.37
21	25	1.5	0.04	1	323	0.107	1.783	66.37
10	26	2	0.025	2.75	333	0.11	1.1	67.29
12	27	2	0.055	2.75	333	0.107	1.783	58.37
9	28	1	0.025	2.75	333	0.08	4	45.71
29	29	1.5	0.04	4.5	323	0.27	2.7	53.21
20	30	1.5	0.07	4.5	323	0.123	2.05	69

X_1= A, X_2 = B, X_3 = C, X_4 = D

3.2 3D surface plots for corrosion rate on zinc

The 3D surface plots interaction between the process variables and response variables.

Plot of the predicted versus actual experimental values for the corrosion rate of BGFE on are shown on Figure 1 gave a linear relationship. Figure 2 presents the interaction effects of the process parameters and their responses on 3D curves. The plots indicates that the inhibition efficiency increased with increase in concentration but decreased with increase in temperature [19-21]. From Table 3 the percentage of the experimental data in relation to standard deviation of the mean and coefficient of variation is 3.09%. The result being lower than 10% indicates that this experiment can be rep reproduced.

Table 3. ANOVA for the corrosion inhibition of winc in HCl by BGFE

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	3063.12	14	218.79	61.83	< 0.0001	significant
A-Acid conc	*150.60*	*1*	*150.60*	*42.56*	*< 0.0001*	
B-Inhibitor concentration	*38.91*	*1*	*38.91*	*11.00*	*0.0047*	
C-Time	*70.52*	*1*	*70.52*	*19.93*	*0.0005*	
D-Temperature	*99.63*	*1*	*99.63*	*28.16*	*< 0.0001*	
AB	*915.37*	*1*	*915.37*	*258.68*	*< 0.0001*	
AC	*59.60*	*1*	*59.60*	*16.84*	*0.0009*	
AD	*87.52*	*1*	*87.52*	*24.73*	*0.0002*	
BC	*207.65*	*1*	*207.65*	*58.68*	*< 0.0001*	
BD	*217.12*	*1*	*217.12*	*61.36*	*< 0.0001*	
CD	*297.22*	*1*	*297.22*	*83.99*	*< 0.0001*	
A^2	*416.92*	*1*	*416.92*	*117.82*	*< 0.0001*	
B^2	*48.06*	*1*	*48.06*	*13.58*	*0.0022*	
C^2	*357.70*	*1*	*357.70*	*101.09*	*< 0.0001*	
D^2	*97.46*	*1*	*97.46*	*27.54*	*< 0.0001*	
Residual	53.08	15	3.54			
Lack of Fit	*46.81*	*10*	*4.68*	*3.73*	*0.0795*	*not significant*
Pure Error	*6.27*	*5*	*1.25*			
Cor Total	3116.20	29				

Std. Dev.	1.88	R-Squared	0.9830
Mean	60.88	Adj R-Squared	0.9671
C.V. %	3.09	Pred R-Squared	0.7506
PRESS	278.63	Adeq Precision	26.097
-2 Log Likelihood	102.25	BIC	153.27
		AICc	166.54

3.3 Predicted Versus Actual Inhibition Efficiency

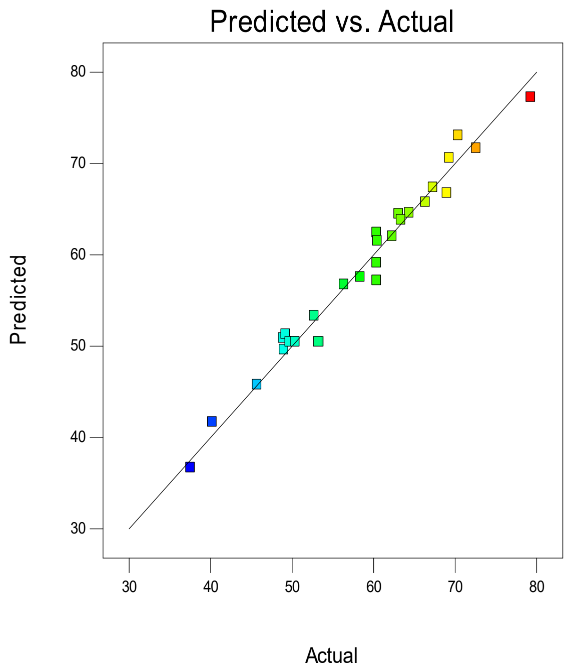
The experimental data was equally analyzed to determine the connection between the experimental (actual) and predicted inhibition efficiency as shown in Fig. 1. The R^2 value of 0.9831 implies that the data points are closely distributed along a straight line. This infers that a good correlation existed between the experimental and predicted values. Conclusively, the regression model is satisfactory for predicting the response variables of the process [12].

3.4 Prediction of optimal levels

The predicted optimal points were acid concentration: 1.0mols, inhibitor concentration 0.055g/l; expose time 6.250 hr and temperature of 333.0K. Validation of the predicted values was done by performing experiments with optimum conditions or points. 81.21% inhibition efficiency confirmed is in reasonable agreement with the experimental data [13-15].

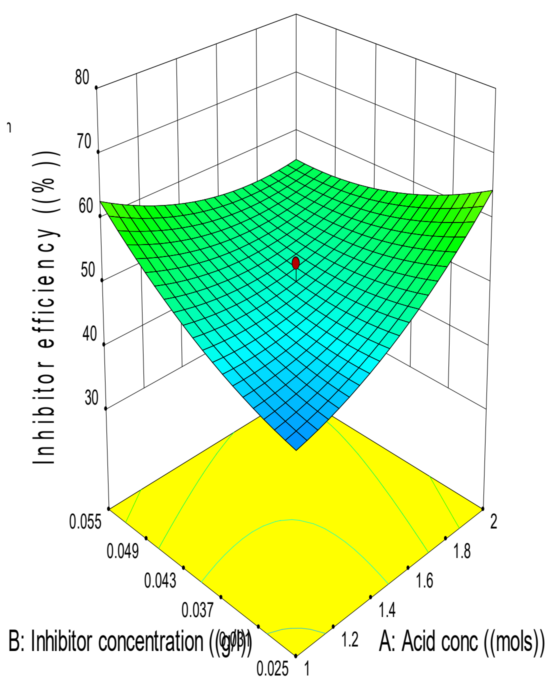
3.5 Result of phytochemical analysis

The result of phytochemical analysis presented on Table 4 reveal the active components in BGFE as alkaloids, flavonoids, saponins, tanins etc improved the inhibiting response of zinc in HCl.

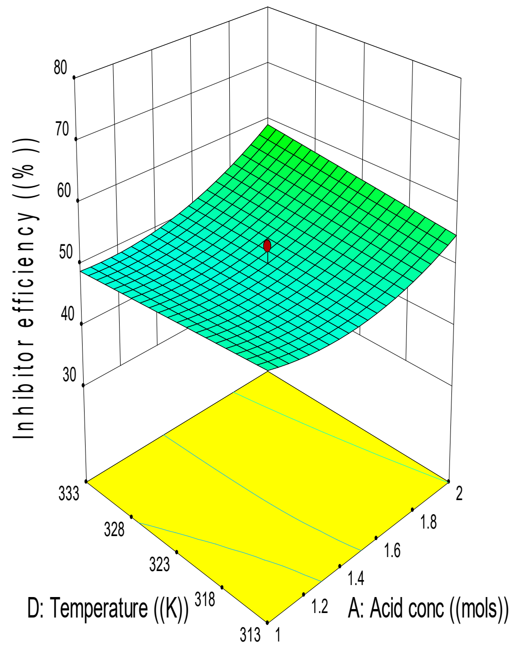


(1)

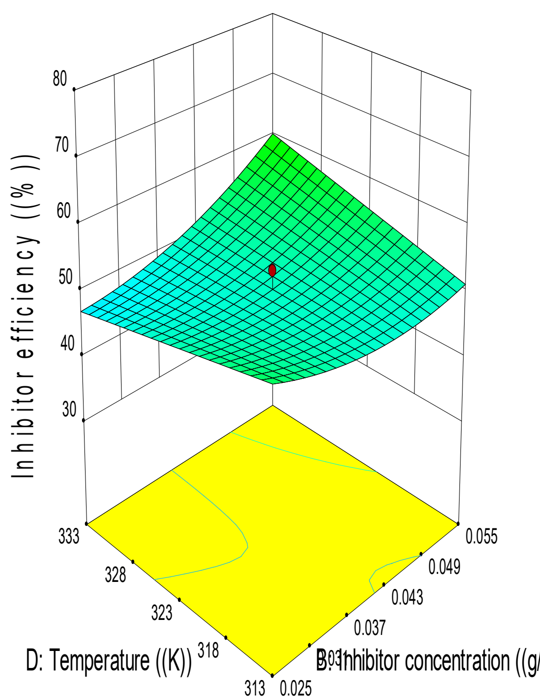
Figure 1: Plot of predicted values versus the actual experimental values for corrosion rate of BGFE on zinc.



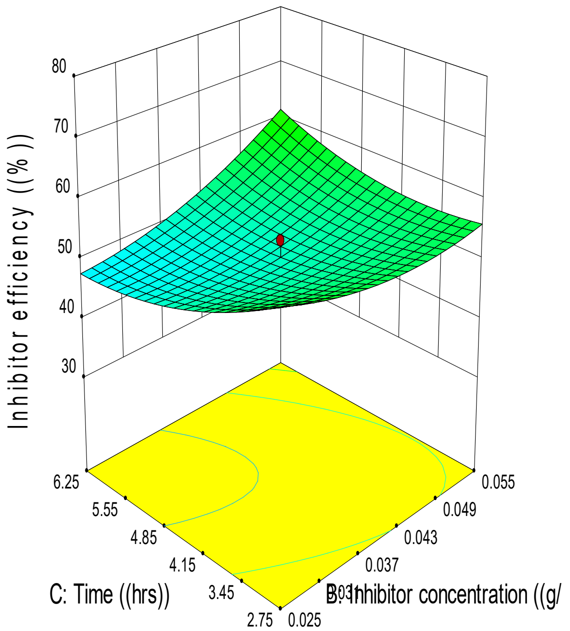
(b)



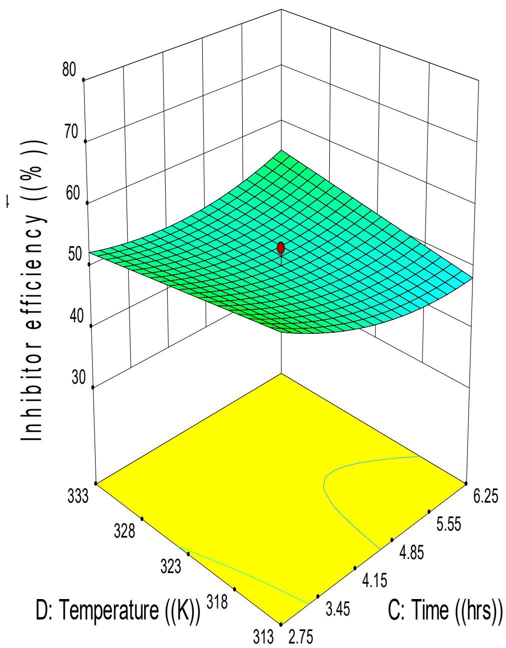
(c)



(d)



(e)



(f)

Figure 2: IE (%) of *Bougainvillea glabra* flower extract as corrosion inhibitor of zinc in HCL.
(a) IE (%) versus inhibitor concentration and acid concentration. (b) IE (%) versus time and acid concentration. (c) IE (%) versus time and inhibitor concentration. (d) IE (%) versus temperature and acid concentration. (e) IE (%) versus temperature and inhibitor concentration. (f) IE (%) versus time and temperature.

Table 4: Phytochemical Analysis of BGFE

Phytochemicals components of BGFE	presence
Alkaloid	+
Terpenoid	+
Steroids	+
Flavonoid	++
Glygoside	+
Tannin	++
Saponins	++
Phlobatannis	+

IV. CONCLUSIONS

Bougainvillea glabra flower extract displayed good inhibition characteristics against zinc corrosion in 2 M HCl medium. *The e*xtract demonstrated its effectiveness and efficiency at both low and high temperatures. The outcome of the results further proved that RSM is appropriate for prediction, modeling and optimization of the inhibition efficiency of *Bougainvillea glabra* flower extract for zince in aggressive HCl environment. In all cases investigated, the inhibition efficiency was affected by the process parameters (extract concentration, acid concentration, and temperature and immersion time). The optimization results obtained unveils that inhibition efficiency of 88.03 % was obtained by combing the values of acid concentration, extract concentration, temperature and immersion time.

REFERENCES

[1]. Uppal, M. M. & Bhatia, S. C., (2009). Engineering chemistry (chemical technology), Khanna publishers, New Delhi, 7th edition, 269-308.
[2]. Punita Mourya, Sitashree Banerjee, & Singh, M.M., (2014), Corrosion inhibition of mild steel in acidic solution by Tagetes erecta (Marigold flower) extracts as a green inhibitor, corrosion Science, 85, 352-363.
[3]. Loveth N. Emembolu*, Dominic O. Onukwuli, Corrosion Inhibitive Efficacy of Natural Plant Extracts on Zinc in 0.5 M HCl Solution, The Pharmaceutical and Chemical Journal, 2019, 6(2):62-70
[4]. https://en.wikipedia.org/wiki/Bougainvillea glabra
[5]. Herborne JB (1973) Phytochemical Methods. 3rd edn. London, Chapman and Hall Ltd., pp: 135-203.
[6]. Odeja O, Obi G, Ogwuche CE, Elemike E E, Oderinlo Y, (2016), Phytochemical Screening, Antioxidant and Antimicrobial activities of Senna occidentalis (L.) Leaves Extract. Journal of Clinical Phytoscience 2, 13.
[7]. Okwu DE, Josiah C (2001) Evaluation of the Chemical Composition of indigenous species and flavouring agents. Global Journal of Pure and Applied Science 7, 455-459.
[8]. Sofowara A (1993) Medicinal Plants and Traditional Medicine in Africa, Ibadan, Nigeria. Spectrum Book.
[9]. Tanvir R, Nawaz R, Zaidi AA, Ruby S, (1994,) Phytochemical Screening of Medicinal Plants belonging to Euphoribiaceae Pak. Veterinary Journal 1, 160-162.
[10]. L. N. Emembolu, O. D. Onukwuli, V. N. Okafor, Characterization and Optimization study of *Epiphyllum*

oxypetalum extract as corrosion inhibitor for mild steel in 3 M H2SO4 solutions, WSN, 145, (2020), 256-273

[11]. Nkuzinna O.C, Menkiti M.C., Onukwuli O.D., Mbah G.O., Okolo B.I., Egbujor M.C., Government R.M., (2014), Application of factorial design of experiment for Optimization of inhibition effect of acid extract of Gnetium Africana on copper corrosion, Natural resources, 5, 299- 307

[12]. Odejobi Oludare J., Akinbulumo Olatunde A., (2019), Modelingand optimization of the inhibition efficiency of *euphorbia heterophylla* extracts based corrosion inhibitor of mild steel corrosion in HCl media using a response surface methodology**,** Journal of Chemical Technology and Metallurgy,54(1), 217-232

[13]. Olawale, O, Bello. Josiah.Olatunde. Ogundipe, Samson.Julius and Abayomi, Tunbosun. Siji and Ogunsemi, B.T, Ikubanni P.P, (2018),Optimization and modelling of aluminium corrosion inhibition using almond (prunus amydgdalus) fruit leaves extract as green inhibitor in HCl acidic medium, International Journal of Mechanical Engineering and Technology, 9(13), 1274–1285, Article ID: IJMET_09_13_12

[14]. Omoruwou F., Okewale A.O. and Owabor C.N., **(**2017), Statistical Analysis of Corrosion Inhibition of Water Hyacinth on Mild Steel in an Acidic Medium, J Environ Anal Toxicol, 7(4), DOI: 10.4172/2161-0525.1000481

[15]. O. Olawale, J.O. Bello, B.T. Ogunsemi, U.C. Uchella, A.P. Oluyori, N.K. Oladejo, (2019),Optimization of chicken nail extracts as corrosion inhibitor on mild steel in 2M H2SO4, Heliyon, 5, e02821