American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-6, Issue-1, pp-344-356
www.ajer.org
Research Paper Open Access

Modelling of Corrosion Inhibition of Mild Steel in Sulphuric Acid by thoroughly Crushed Leaves of Voacanga Africana (Apocynaceae)

Agha Inya Ndukwe[1] and C. N. Anyakwo[2]

[1] *Department of Metallurgical Engineering Technology, Akanu Ibiam Federal Polytechnic Unwana, P.M.B. 1007, Afikpo, Nigeria.*

[2] *Department of Materials and Metallurgical Engineering, Federal University of Technology, P.M.B. 1526, Owerri, Nigeria.*

ABSTRACT: *The inhibition of the corrosion of mild steel in 0.7M, 1.2M and 2.2M H_2SO_4 by thoroughly crushed fresh leaves of Voacanga Africana was studied using the weight-loss technique. The addition of the crushed leaves of Voacanga Africana at 30g per litre of 1.2M H_2SO_4 gave the highest average inhibition efficiency of 88.69% while the corrosion rate decreased from 2.9247mgcm^{-2}h^{-1} to 0.6313mgcm^{-2}h^{-1}. The corrosion rate was observed to increase with increase in the concentration of acid. Predictions by the artificial neural network produced minimal errors and were closer to the experimental corrosion rate values in comparison with predictions by multiple regression. The protective film formed on the mild steel surface was analyzed by FTIR spectroscopy and surface electron microscopy (SEM). The FTIR spectrum of the adhered constituents of Voacanga Africana's pounded leaves on the surface of mild steel coupon immersed at 30g per litre of 0.7M H_2SO_4 for eight hours indicates the presence of stretching vibrations of C≡C, C=C and C=O bonds. The SEM image shows that the degradation of the surface of mild steel in an uninhibited solution of 0.7M H_2SO_4 is localized but the surface of the steel is remarkably protected by the addition of the crushed leaves of Voacanga Africana at 30g per litre of 0.7M H_2SO_4. Four adsorption isotherm models were tested and the results show that the corrosion inhibition of mild steel in H_2SO_4 by the pounded leaves of Voacanga Africana strongly obeys the Langmuir adsorption isotherm model with R^2=0.999. The phytochemical analysis of the leaves of Voacanga Africana reveals the presence of alkanoid, flavonoid, phytate, tannin and saponin.*

Keywords: *oacanga Africana; Thoroughly crushed leaves; Corrosion rate; Inhibition efficiency; Artificial neural network; Multiple regression*

I. INTRODUCTION

Metals corrode because we use them in environments where they are chemically unstable (Why Metals Corrode, n.d.). Corrosion is a potent force which destroys the economy, depletes resources and causes costly and untimely failures of plants, equipment and components (Ahmed, 2006, p. 3). Corrosion happens through a series of reactions; the metal being corroded acts as the anode thus, forming metal ions and free electrons. On the other hand, the free electrons reduce the oxygen, often times forming hydroxide and providing a complimentary cathodic reaction (Escobar and Cantu, n.d). Carbon steel being one of the most common alloys that is used in the construction industry is not immune from corrosion.

Depending upon the carbon content, steels are classified as mild steels, medium carbon steels and high carbon steels. In mild steel, the carbon content varies from 0.15 to 0.30%. Mild steels are quite tough, ductile, and can be permanently magnetized. They have good shock and impact resistance and are difficult to be hardened and tempered. They undergo corrosion very rapidly and are not much affected by saline water (Sharma, 2011). The corrosion of steel can be prevented by cathodic protection technique, painting, electroplating and addition of inhibitors.

Majority of corrosion inhibitors are synthetic chemicals, expensive and very hazardous to the environment. This concern has made it imperative to seek an alternative method of inhibition that is not just environmentally friendly but less expensive. Previous work has shown that products of plant origin contain different organic compounds like alkanoids, tannins, pigments and amino acids which are known to have some inhibitive action (Kumar et al, 2014). This present study is concerned with corrosion inhibition by the leaves of Vocanga Africana.

Voacanga Africana (Apocynaceae) is a small African tree that grows to *6mm* in height. It has leaves that are up to *30cm* in length, and the tree produces yellow or white flowers which become berries with yellow seeds. The various species of the genus are very similar to one another, featuring yellow or white flowers with five united petals. The bark contains latex (Hofmann et al., 1992).

Experimental outcomes can be predicted by comparing the dependent variable parameter with independent-designate parameters. This development can be achieved by employing the artificial neural network and multiple regression.

This present study seeks to:

(1) Investigate the effectiveness of thoroughly crushed leaves of Voacanga Africana in inhibiting the corrosion of mild steel immersed in sulphuric acid medium.

(2) Develop a model that can predict the experimental corrosion rate -resulting from the inhibition.

(3) Figure out the adsorption isotherm that the inhibitor obeys in sulphuric acid medium.

II. MATERIALS AND METHODS

2.1 Preparation of Plant Extract

The fresh leaves of Voacanga Africana were obtained within the University (Federal University of Technology Owerri) environment and thoroughly pounded using a manual blender and added to the study environment at 15g per litre, 30g per litre and 45g per litre of 0.7M, 1.2M and 2.2M H_2SO_4.

2.2 Preparation of Mild Steel Coupons

Mild steel ((wt %) C=0.20%, Zn=0.75%, Ti=0.28, Mn=0.23%, S=0.04%, P=0.035% and Fe balance) coupons of $40mm \times 40mm$ dimensions were press cut from a sheet metal of 1.5mm thickness using a foot shear cutting machine.

2.3 Weight–loss Measurement

Mild steel coupons were immersed in a bowl containing the acid solution where the thoroughly crushed leaves of Voacanga Africana had been added at 15g per litre, 30g per litre and 45g per litre of 0.7M, 1.2M and 2.2M H_2SO_4. Another experimental set-up with no inhibitor was prepared for the purpose of comparison. Each experiment lasted for eight hours and in each hour; a coupon was withdrawn from the acidic medium, cleaned with acetone, allowed to dry and re-weighed with the ohaus electronic weighing balance. In addition, the moisture content of the fresh leaves of Voacanga Africana as at the time of experimentation was 70.71%.

The corrosion rate was computed using the relationship (Khadom, 2014):

Corrosion rate, $CR = \frac{w}{A \times t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ (1)

Where,

w = *Weight loss,*

A = Exposed area, and

t = Exposure time.

On the other hand, the inhibition efficiency was figured out using the equation (Roberge, 2000):

$$I.E(\%) = \frac{CR_{uninhibited} - CR_{inhibited}}{CR_{uninhibited}} \times 100 \ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where,

$CR_{uninhibited}$ = *Corrosion rate of the uninhibited system*

$CR_{inhibited}$ = *Corrosion rate of the inhibited system.*

2.4 Model Development

2.4.1 Multiple Regression

The purpose of multiple regression is to predict a single variable from one or more independent variables. In other words, it is a powerful method to analyze multivariate data (Stockburger, n.d.). The prediction of Y is accomplished by the equation below:

$$Yi = b_o + b_1X_{1i} + b_2X_{2i} + \ldots + b_kX_{ki} \ldots\ldots\ldots\ldots\ldots \quad (3)$$

In the present study, equation (3) is better stated thus:

$$Yi = b_o + b_1(time) + b_2(conc.of\ acid) + b_3(quantity\ of\ crushed\ leaves) \ldots.. \quad (4)$$

Where,

Yi= the predicted value of Y (which is the experimental corrosion rate).

b_o = *the 'Y intercept'.*

b_1 = *the change in Y for each 1 increment change in* X_{1i}.

b_2 = *the change in Y for each 1 increment change in* X_{2i}.

X_{1i} = an X score on your first independent variable for which you are trying to predict a value of Y.
X_{2i} = an X score on your second independent variable for which you are trying to predict a value of Y.

2.4.2 Artificial Neural Network

Artificial neural networks are inspired by our present knowledge of biological nervous systems, although they do not try to be realistic in every detail. Artificial neural networks (ANN), also called neurocomputing, connectionism, or parallel distributed processing (PDP), provide an alternative approach to be applied to problems where the algorithmic and symbolic approaches are not well suited (Artificial Neural Network, n.d.).

According to (Fausett, n.d., p. 3), artificial neural networks have been developed as generalizations of mathematical models of human cognition or neural biology, based on the assumptions that: Information processing occurs at many simple elements called neurons; Signals are passed between neurons over connection links; Each connection link has an associated weight, which, in a typical neural net, multiplies the signal transmitted; and each neuron applies an activation function to its net input to determine its output signal. In other words, a neural network is characterized by its pattern of connections between the neurons (called its architecture); its method of determining the weights on the connections (called its training or learning algorithm) and its activation function. Figure 1 highlights the data processing of a neuron whereas the artificial neural network diagram for the prediction of corrosion inhibition of mild steel by the crushed leaves of Voacanga Africana is given in Figure 2.

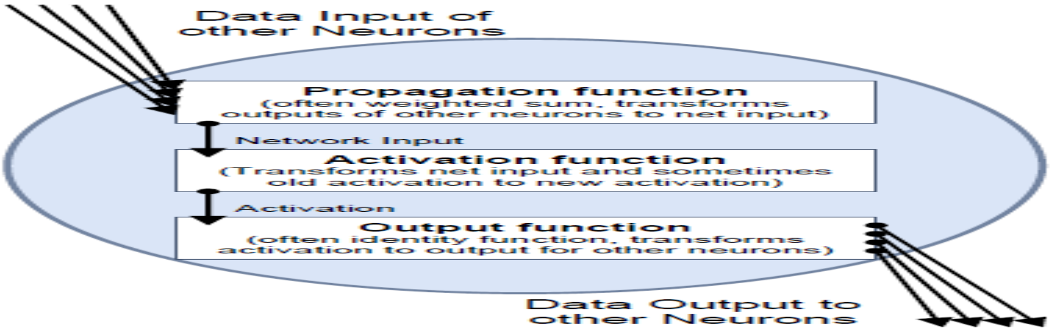


Figure 1: Data processing of a neuron (Kriesel, 2005).

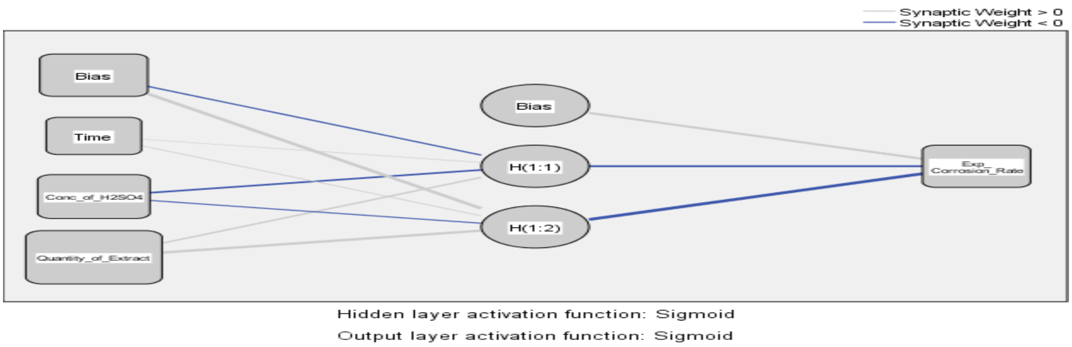


Figure 2: Artificial neural network diagram for the prediction of corrosion inhibition of mild steel by the crushed leaves of Voacanga Africana

The net output, y_j is given by (Fausett, n.d.):

$$y_j = f(y\_in_j) \qquad (5)$$

$$y\_in_j = b_j + \sum_i x_i w_{ij} \qquad (6)$$

$$f(x) = \frac{1}{1 + \exp(-x)} \qquad (7)$$

Where,
f = activation function.
y_in_j = net input to unit Y_j.
bj = bias of the unit.

2.4.3 Evaluation of Error in Prediction

The mean absolute error (MAE) and mean squared error (MSE) are used to figure out how close a predicted value is to the actual value. Mathematically, the mean squared error is represented thus (Mean Squared Error and Residual Sum of Squares, 2013):

$$MSE = \frac{1}{N}\sum(f_i - y_i)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where,

N = *number of samples.*

f_i = *an estimator of parameter* y_i.

y_i = *true value.*

The formula for computing the mean absolute error is given by (Mean Absolute Error, 2016):

$$MAE = \frac{1}{n}\sum_{i=1}^{n}|f_i - y_i| \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where,

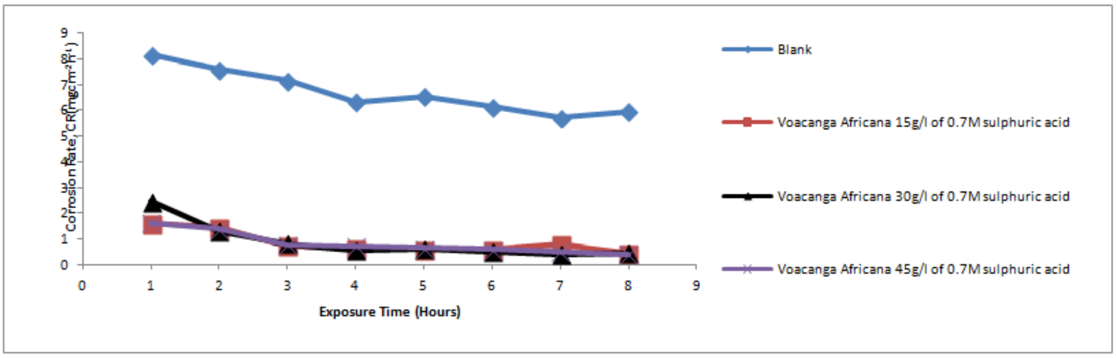
f_i = *t□e predicted/forecasted value.*

y_i = *t□e true/observed value.*

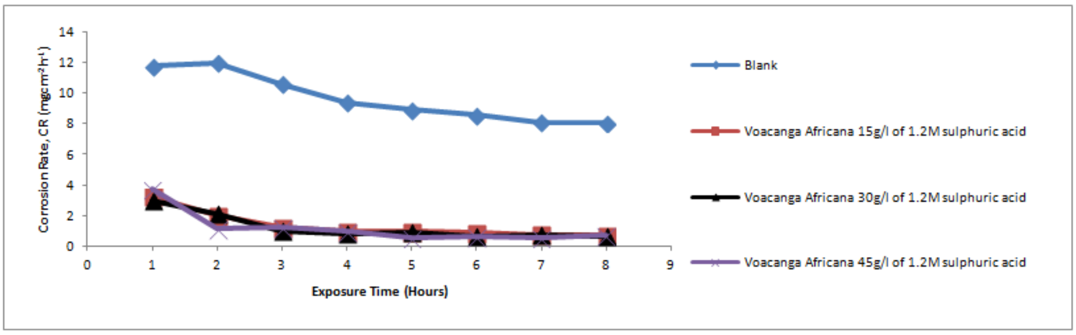
III. RESULTS

Table 1: Effect of addition of thoroughly crushed fresh leaves of Voacanga Africana on the corrosion of mild steel coupons immersed in sulphuric acid solution

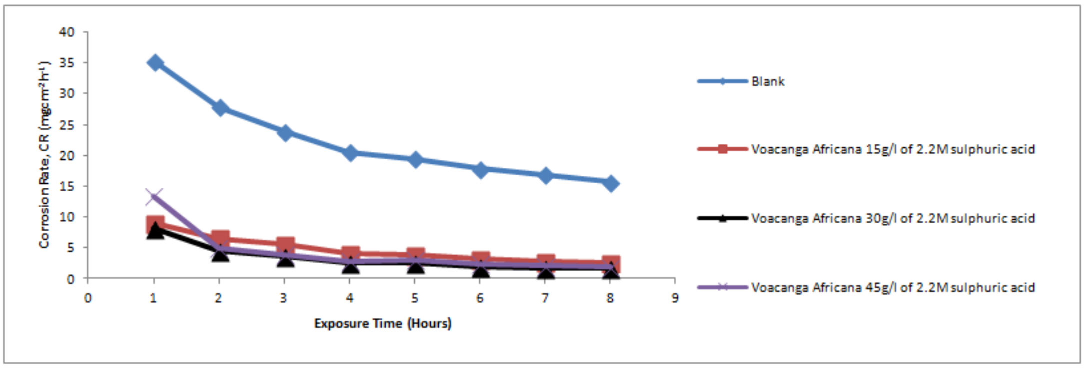
Exposure Time (h)	0.7M H_2SO_4		1.2M H_2SO_4		2.2M H_2SO_4	
	CR ($mgcm^{-2}h^{-1}$)	I.E (%)	CR ($mgcm^{-2}h^{-1}$)	I.E (%)	CR ($mgcm^{-2}h^{-1}$)	I.E (%)
Addition of crushed leaves of Voacanga Africana at 15g per litre of H_2SO_4						
1	1.6322	80.05	3.2209	72.64	9.1109	74.25
2	1.4464	80.95	1.9982	83.92	6.5318	76.55
3	0.7271	89.85	1.2072	88.61	5.5666	76.67
4	0.6346	89.97	0.9642	89.75	4.0363	80.38
5	0.6175	90.55	0.9375	89.49	3.9307	79.76
6	0.5872	90.42	0.8679	89.90	3.1686	82.23
7	0.8082	85.83	0.7435	90.81	2.7612	83.60
8	0.4433	92.54	0.6821	91.56	2.5634	83.61
Average	**0.8621**	**87.52**	**1.3277**	**87.09**	**4.7087**	**79.63**
Addition of crushed leaves of Voacanga Africana at 30g per litre of H_2SO_4						
1	2.4512	70.04	2.9247	75.15	8.2918	76.56
2	1.3171	82.65	2.0780	82.65	4.5482	83.67
3	0.8432	88.22	0.9633	90.91	3.7475	84.30
4	0.5453	91.38	0.8314	91.16	2.5979	87.37
5	0.6111	90.65	0.8940	90.50	2.4884	87.19
6	0.5112	91.66	0.6530	96.21	1.8844	89.43
7	0.3850	93.25	0.7481	90.75	1.7833	89.41
8	0.4393	92.61	0.6313	92.19	1.7132	83.69
Average	**0.8879**	**87.56**	**1.2155**	**88.69**	**3.3818**	**85.20**
Addition of crushed leaves of Voacanga Africana at 45g per litre of H_2SO_4						
1	1.6351	80.01	3.7117	68.47	13.3512	62.26
2	1.3796	81.82	1.1690	90.24	4.9504	82.23
3	0.7820	89.06	1.2285	88.41	3.8899	83.70
4	0.7384	88.33	0.9860	89.52	2.8942	85.94
5	0.6668	89.78	0.5309	94.05	3.1158	83.96
6	0.5814	90.51	0.6627	92.29	2.4721	86.14
7	0.5137	91.00	0.5594	93.08	2.0575	87.78
8	0.4132	93.05	0.7072	91.25	1.8577	88.12
Average	**0.8389**	**87.95**	**1.1944**	**88.41**	**3.0736**	**82.52**



(a)



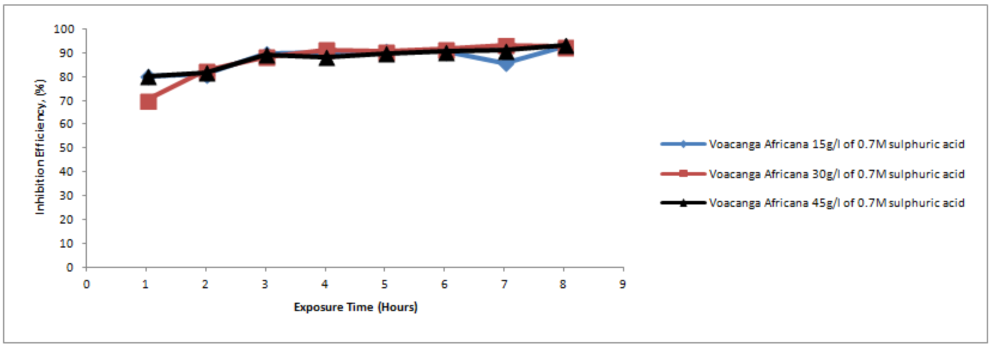
(b)



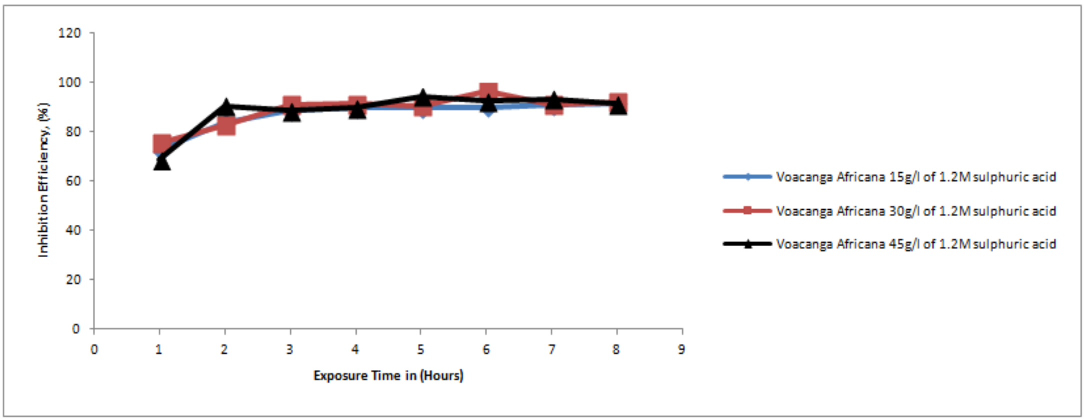
(c)

Figure 3: Effect of addition of thoroughly crushed leaves of Voacanga Africana on corrosion of mild steel coupons immersed at:

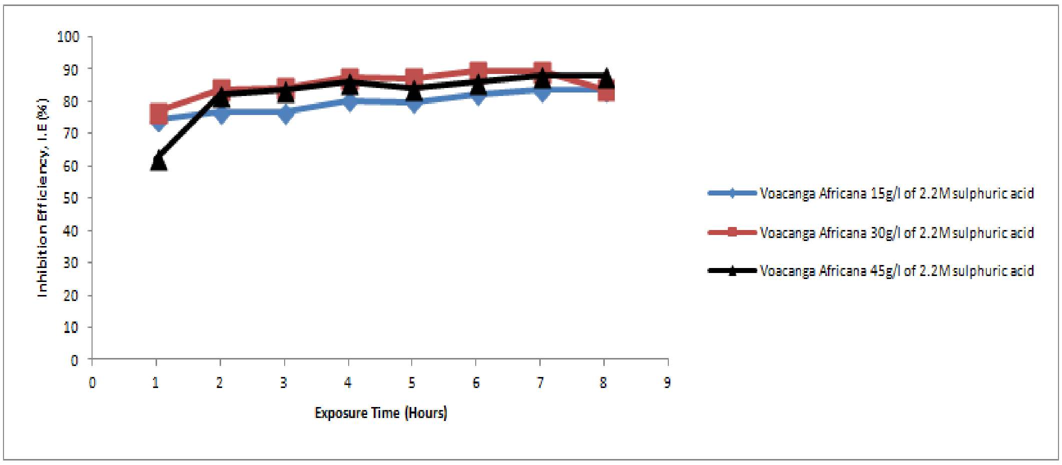
(a) 15g/l, 30g/l and 45g/l of 0.7M H_2SO_4
(b) 15g/l, 30g/l and 45g/l of 1.2M H_2SO_4
(c) 15g/l, 30g/l and 45g/l of 2.2M H_2SO_4



(a)



(b)



(c)

Figure 4: Voacanga Africana's corrosion inhibition efficiency for mild steel coupons immersed at:
(a) 15g/l, 30g/l and 45g/l of 0.7M H_2SO_4
(b) 15g/l, 30g/l and 45g/l of 1.2M H_2SO_4
(c) 15g/l, 30g/l and 45g/l of 2.2M H_2SO_4

Table 2: Analysis for prediction of corrosion inhibition of mild steel by thoroughly pounded fresh leaves of Voacanga Africana in sulphuric acid medium using multiple regression (MR)

	Model Coefficients			
	Constant	**Time (h)**	**Conc. of Acid (M)**	**Quantity of Crushed Leaves (g)**
H_2SO_4	6.597	-0.644	4.371	-0.218

Table 3: Analysis for prediction of corrosion inhibition of mild steel by thoroughly crushed fresh leaves of Voacanga Africana in sulphuric acid solution using artificial neural network (ANN)

Independent variable importance for the addition of crushed leaves of Voacanga Africana in sulphuric acid

	Importance	Normalized Importance
Time	0.149	27.5%
Conc_of_H_2SO_4	0.310	57.4%
Quantity_of_Extract	0.541	100.0%

Parameter estimates for the addition of crushed leaves of Voacanga Africana in sulphuric acid

Predictor		Predicted		
		Hidden Layer 1		Output Layer
		H(1:1)	H(1:2)	Exp_Corrosion_Rate
Input Layer	(Bias)	-0.796	4.521	
	Time	0.297	0.432	
	Conc_of_H_2SO_4	-1.485	-0.791	
	Quantity_of_Extract	1.125	2.840	
Hidden Layer 1	(Bias)			2.795
	H(1:1)			-1.638
	H(1:2)			-5.064

Table 4: Error analysis for the prediction of corrosion inhibition of mild steel by thoroughly crushed leaves of Voacanga Africana in sulphuric acid using multiple regression, MR and artificial neural network, ANN

Error	Prediction of CR by Multiple Regression, MR	Prediction of CR by Artificial Neural Network, ANN
Mean Absolute Error	2.949091354	1.272221875
Mean Squared Error	17.2004801	3.490951204

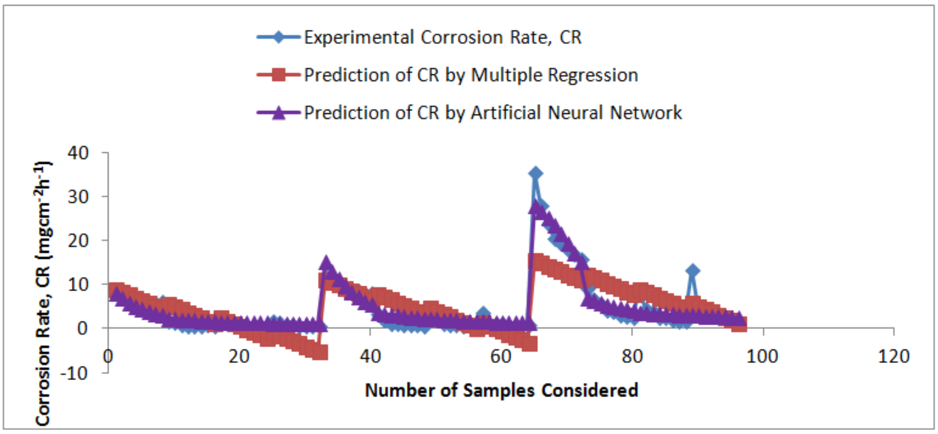


Figure 5: Comparison of error for the prediction of corrosion inhibition of mild steel by crushed leaves of Voacanga Africana in sulphuric acid using multiple regression, MR and artificial neural network, ANN

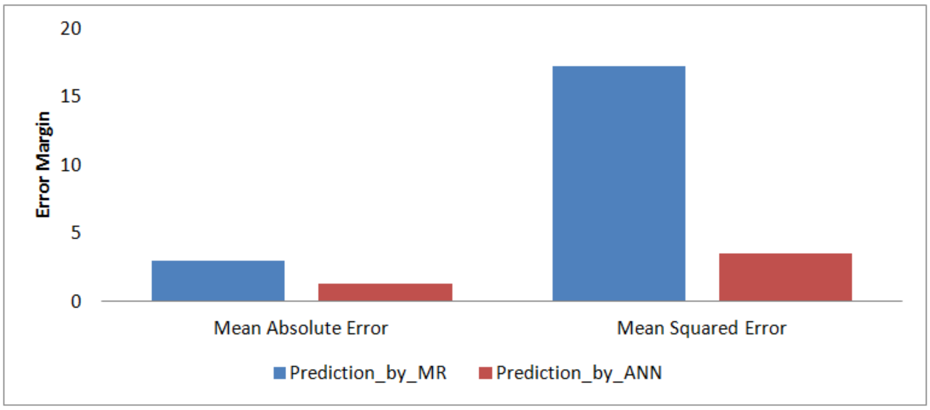


Figure 6: Error graph for the prediction of corrosion inhibition of mild steel by crushed leaves of Voacanga Africana in sulphuric acid solution using multiple regression, MR and artificial neural network, ANN

Table 5: Effect of variation in temperature on the corrosion of mild steel coupons immersed in 0.7M H_2SO_4 without and with 15g of crushed Voacanga Africana's fresh leaves

Temperature (K)	**$CR_{VA\ addition}$ ($mgcm^{-2}h^{-1}$)**	**CR_{Blank} ($mgcm^{-2}h^{-1}$)**	**Log $CR_{VA\ addition}$**	**Log CR_{Blank}**	**1/T (K^{-1})**
298	0.8621	6.6966	-0.0644	0.8259	0.003356
318	4.0379	14.9549	0.6062	1.1748	0.003145
338	4.0149	13.6092	0.6037	1.1447	0.002959
358	5.4304	14.3791	0.7348	1.1577	0.002793

$Slope_{Blank}$ = $-528.9K^{-1}$
Activation Energy, Q = 10,126.92J

$Slope_{VA\ addition}$ = $-1{,}309K^{-1}$
Activation Energy, Q = 25,063.61J

$Slope_{VA\ addition}$ = Slope for the addition of crushed leaves of Voacanga Africana at 15g per litre of 0.7M H_2SO_4

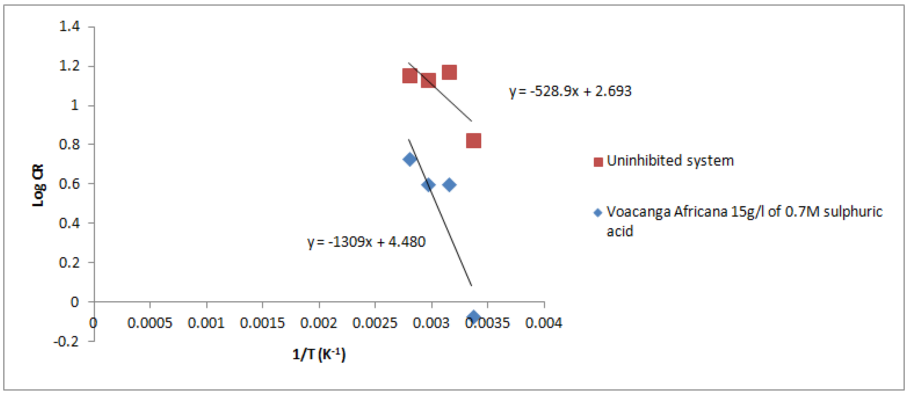
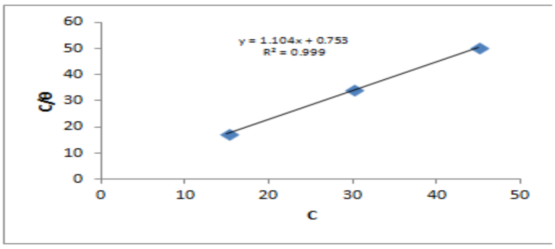


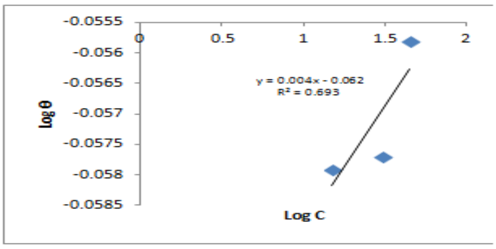
Figure 7: Arrhenius plot for the effect of addition of thoroughly crushed fresh leaves of Voacanga Africana to sulphuric acid induced corrosion of mild steel coupons immersed at 15g per litre of 0.7M H_2SO_4

Table 6: Calculated parameters of four adsorption isotherm models for adsorption of crushed fresh leaves of Voacanga Africana onto the surface of mild steel coupons in sulphuric acid medium.

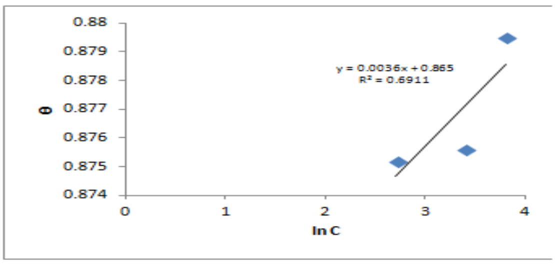
Adsorption Isotherm							
Langmuir		**Freundlich**		**Temkin**		**El-Awady**	
Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2
1.104	0.999	0.004	0.693	0.003	0.691	0.032	0.690
Parameters							
C (g)	**Log C**	**In C**	**□**	**C/ □**	**Log □**	**1- □**	**Log (□/1- □)**
15	1.1761	2.7081	0.8752	17.1389	-0.0579	0.1248	0.8459
30	1.4771	3.4012	0.8756	34.2622	-0.0577	0.1244	0.8475
45	1.6532	3.8067	0.8795	50.2793	-0.0558	0.1205	0.8632



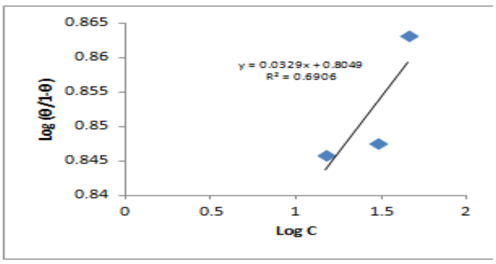
(a)



(b)



(c)



(d)

Table 7: Result of the phytochemical analysis conducted on the leaves of Voacanga Africana

Plant Leaf		Compounds					
		Saponin (%)	Tanin (%)	Flavonoid (%)	Alkanoid (%)	Phytate (%)	Phenol (ppm)
Voacanga Africana	Dry	2.81	1.957	4.70	4.10	0.586	22.19
	Fres□	1.05	0.471	1.60	3.00	0.284	18.04

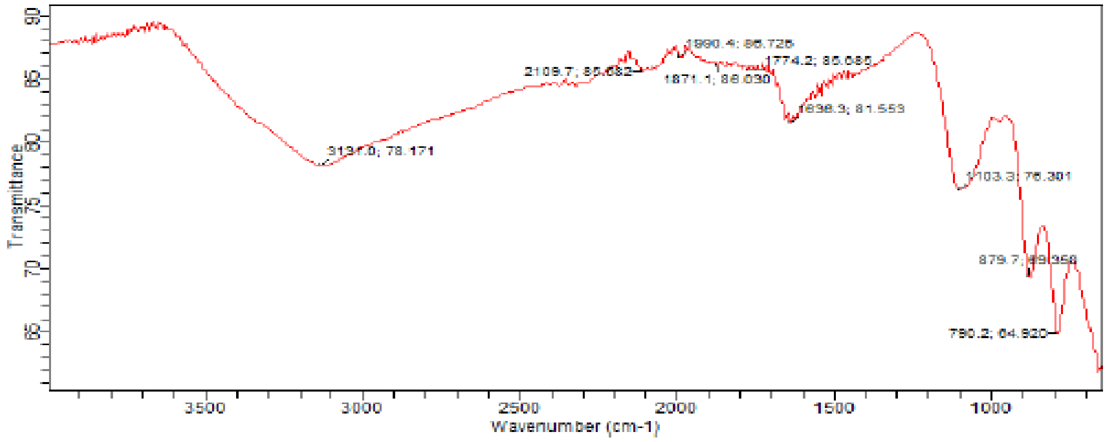


Figure 9: FTIR Spectrum of film on mild steel surface after immersion for eight hours in a medium containing crushed fresh leaves of Voacanga Africana at 30g per litre of 0.7M H_2SO_4

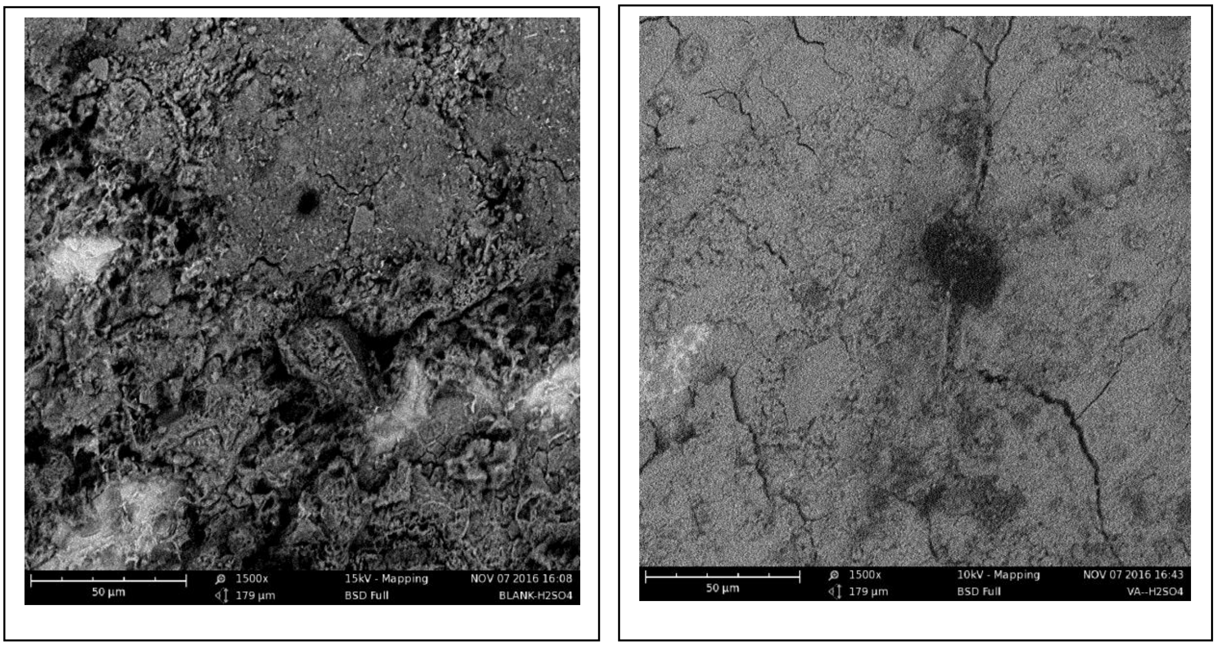


Figure 10: SEM characteristics of the corroded mild steel in; (a) the blank solution of 0.7M H_2SO_4 (b) the presence of thoroughly crushed leaves of Voacanga Africana at 30g per litre of 0.7M H_2SO_4

IV. DISCUSSION OF RESULTS

4.1 Effect of addition of thoroughly pounded leaves of Voacanga Africana on the corrosion of mild steel coupons immersed in sulphuric acid medium

The addition of thoroughly crushed leaves of Voacanga Africana at 15g per litre of 0.7M, 1.2M and 2.2M H_2SO_4 gave the following average corrosion rate, CR and inhibition efficiency, I.E in the order CR (I.E) as illustrated in Table 1: 0.8621$mg\,cm^{-2}\square^{-1}$ (87.52%) in 0.7M H_2SO_4; 1.3277$mg\,cm^{-2}\square^{-1}$ (87.09%) in 1.2M H_2SO_4 and 4.7087 $mg\,cm^{-2}\square^{-1}$ (79.63%) in 2.2M H_2SO_4. As the addition of the inhibitor was increased to 30g per litre of various acid concentrations, the corresponding average corrosion rate and inhibition efficiency were: 0.8879$mg\,cm^{-2}\square^{-1}$ (87.56%) in 0.7M H_2SO_4; 1.2155$mg\,cm^{-2}\square^{-1}$ (88.69%) in 1.2M H_2SO_4 and 3.3818 $mg\,cm^{-2}\square^{-1}$ (85.20%) in 2.2M H_2SO_4. Further addition of the inhibitor at 45g per litre of different acid solutions gave the following average corrosion rate and inhibition efficiency: 0.8389$mg\,cm^{-2}h^{-1}$ (87.95%) in 0.7M H_2SO_4; 1.1944$mg\,cm^{-2}h^{-1}$ (88.41%) in 1.2M H_2SO_4 and 3.0736$mg\,cm^{-2}h^{-1}$ (82.52%) in 2.2M H_2SO_4. The addition of the crushed leaves of Voacanga Africana reduced the corrosion of mild steel coupons in H_2SO_4. In addition, the corrosion rate was observed to increase with increase in the concentration of acid whilst the inhibition efficiency improved with time.

Figure 3 shows the corrosion rate–time curves for the mild steel coupons immersed in 0.7M, 1.2M and 2.2M H_2SO_4 with and without Voacanga Africana's crushed fresh leaves. The corrosion rate curves decreased progressively as the exposure time increased. It can also be seen from Figure 3 that the corrosion rate of mild steel, in the entire study environment, is lower in the presence of the inhibitor than in the blank acid solution. This development suggests the presence of some inhibitive constituents in the fresh-leaf extract of Voacanga Africana which inarguably reduce the corrosion rate of mild steel in sulphuric acid medium.

The inhibition efficiency–time curves for mild steel coupons as a result of the addition of the inhibitor at 15g per litre, 30g per litre and 45g per litre of 0.7M, 1.2M and 2.2M H_2SO_4 corrodents are shown in Figure 4. The inhibition efficiency was observed to improve with time. This further shows that the inhibitive constituents in the crushed leaves, with time, adhere to the surface of the mild steel to prevent the degradation of the steel as confirmed by the Langmuir, Freundlich, Temkin and El-Awady adsorption isotherms (Figure 8). The maximum inhibition efficiency of 88.69% was achieved by the addition of thoroughly crushed leaves of Voacanga Africana at 30g per litre of 1.2M H_2SO_4.

4.2 Prediction of corrosion inhibition of mild steel in sulphuric acid by the crushed leaves of Voacanga Africana

Multiple regression and artificial neural network were used to predict the corrosion rates of mild steel coupons with and without the addition of the crushed leaves of Voacanga Africana in sulphuric acid solution. The predicted values are presented in Appendix 1. Using multiple regression as illustrated in Table 2, the predictive equation for the addition of the crushed leaves of Voacanga Africana to sulphuric acid solution is given thus:

$$CR_{VA\ in\ H_2SO_4\ by\ MR} = 6.597 - 0.644(\text{time}) + 4.371(\text{conc. of acid}) - 0.218(\text{quantity of crushed leaves}) \quad \ldots\ldots\ldots. \quad (10)$$

On the other hand, the prediction of the experimental corrosion rate by the artificial neural network revealed the importance of independent variables namely: (time (h), concentration of acid (M) and quantity of crushed leaves (g)) in the prediction of the dependent variable (Corrosion rate, CR ($mgcm^{-2}h^{-1}$) as illustrated in Table 3 whilst the network is shown in Figure 2. It was observed that the quantity of extract greatly influenced the experimental corrosion rate prediction by 54.1%, followed by concentration of acid, 31.0% and lastly the time of exposure, 14.9%.

The mean absolute error (MAE) and mean squared error (MSE) were used to investigate how close the predicted value was to the actual value. The comparison of error results for the prediction of corrosion inhibition of mild steel by Voacanga Africana's crushed leaves in sulphuric acid solution using multiple regression and artificial neural network are presented in Table 4 and displayed in Figures 5 and 6. The results show that the predictions by the artificial neural network gave a minimal error and were closer to the experimental corrosion rate values in comparison with the predictions by multiple regression.

4.3 Effect of Temperature

Results of variation in temperature between 298K and 358K on the corrosion of mild steel without and with the addition of thoroughly crushed leaves of Voacanga Africana at 15g per litre of 0.7M H_2SO_4 are presented in Table 5 and shown in Figure 7. The activation energy for the corrosion of mild steel in the un-inhibited solution of 0.7M H_2SO_4 was 10,126.92J whilst the addition of the inhibitor at 15g per litre of 0.7M H_2SO_4 increased the activation energy to 25,063.61J. The greater value of activation energy obtained by the introduction of the inhibitor to the corrodent suggests that higher energy needs to be reached before further corrosion can take place.

4.4 Adsorption Isotherm

Langmuir, Freundlich, Temkin and El-Awady adsorption isotherm models were tested and presented in Table 6 and Figure 8. The results show that the corrosion inhibition of mild steel, occasioned by the addition of thoroughly crushed leaves of Voacanga Africana obeys all the aforementioned adsorption isotherms with the Langmuir adsorption isotherm maintaining the best fit of R^2=0.999; Freundlich, R^2=0.693; Temkin, R^2=0.691; and El-Awady isotherm, R^2=0.690. The equations of the aforementioned adsorption isotherms are given below (Adejo et al., 2013; Fadare et al., 2016):

Langmuir: $\frac{C}{\theta} = C + \frac{1}{K}$ ……………………………………………… (11)

Freundlich: $\log\theta = \log K + n\log C$ ………………………………...... (12)

El-Awady: $\log\left(\frac{\theta}{1-\theta}\right) = \log K + y\log C$ ………………………….......... (13)

Temkin: $\theta = b\ln A + b\ln C$ ……………………………………………... (14)

Where,

θ is the fraction of surface coverage.

C is the inhibitor concentration.

K is the equilibrium constant for the adsorption/desorption process.

b = Constant related to heat of sorption (J/mol).

The Langmuir adsorption isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. On the other hand, the Freundlich adsorption isotherm is commonly used to describe the adsorption characteristics of a heterogeneous surface whilst Temkin's model is characterised by a uniform distribution of binding energies (Dada et al., 2012).

4.5 Phytochemical Analysis of the Leaves of Voacanga Africana

The phytochemical analysis of Voacanga Africana's leaves as presented in Table 7 reveals the presence of alkanoid (4.10%), tannin (1.957%), saponin (2.81%), phytate (0.586%), flavonoid (4.70%) and phenol (22.19ppm)**.** These natural constituents may be responsible for adsorbing on the surface of the mild steel thereby effecting corrosion inhibition.

4.6 FTIR Analysis

The FTIR spectrum of the adhered constituents of crushed leaves of Voacanga Africana on the surface of mild steel coupon immersed at 30g per litre of 0.7M H_2SO_4 for eight hours is shown in Figure 9. The sharp peak at the frequency, 2109.7cm^{-1} indicates the presence of triple carbon-carbon stretching of alkynes. The strong bands show that the alkynes are asymmetrical in nature. The C=O stretching of an acid anhydride is depicted around 1774.2cm^{-1}. The double carbon-carbon stretching of alkenes is seen at 1636.3cm^{-1}.

4.7 Micrograph of the Corroded Mild Steel

The SEM image shows that the degradation of the surface of mild steel in an uninhibited solution of 0.7M H_2SO_4 is localized but the surface of the steel is remarkably protected by the addition of thoroughly crushed leaves of Voacanga Africana at 30g per litre of 0.7M H_2SO_4 as displayed in Figure 10(b)

V. CONCLUSION

1. The addition of thoroughly crushed leaves of Voacanga Africana reduced the corrosion of mild steel. The corrosion rate was observed to increase with increase in the concentration of acid whilst the inhibition efficiency improved with time. The maximum inhibition efficiency of 88.69% was achieved by the addition of thoroughly crushed leaves of Voacanga Africana at 30g per litre of 1.2M H_2SO_4.
2. The mean absolute error (MAE) and mean squared error (MSE) were used to investigate how close the predicted value was to the actual value. The results show that predictions by the artificial neural network gave a minimal error and were closer to the experimental corrosion rate values in comparison with the predictions by multiple regression.
3. Four adsorption isotherms were tested and the results show that the corrosion inhibition of mild steel in H_2SO_4 by the pounded leaves of Voacanga Africana strongly obeys the Langmuir adsorption isotherm model with R^2=0.999.
4. The phytochemical chemical analysis of the leaves of Voacanga Africana reveals the presence of alkanoid, flavonoid, phytate, tannin and saponin.
5. The FTIR spectrum of the adhered constituents of thoroughly crushed leaves of Voacanga Africana on the surface of mild steel coupon immersed at 30g per litre of 0.7M H_2SO_4 for eight hours indicates the presence of stretching vibrations of C≡C, C=C and C=O bonds.

REFERENCES

[1]. Escobar, K. & Cantu, L. A. (n.d). Retrieved May 4, 2015, from http://www.chem
[2]. wiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/case_Studies/Corrosion_Basics
[3]. Why Metals Corrode. (n.d.). Retrieved May 2, 2015, from http://www.corrosion.
[4]. ksc.nasa.gov/corr_metal.htm
[5]. Ahmed, Z. (2006). Corrosion Engineering and Corrosion Control (pp.1-8, 58, 352).
[6]. USA: Elsevier Science and Technology Books.
[7]. Kumar, C., Mohan, R., Amalraj, A. J., Peter, A., Regis, P., Rajarathinam, C., Sel- varaj, S. K., Sakthivel, S. & Sahayaraj, J. W. (2014). Anti-Corrosive Effect of Tridax Procumbens–Zn^{2+} System Controlling the Corrosion of Carbon Steel. Journal of Engineering Research and Applications, Vol. 4, Issue 3 (Version 6), pp.06-12
[8]. Sharma, B. K. (2011): Industrial Chemistry (Including Chemical Engineering) (p. 1698-1708). India:Krishna Press.
[9]. Adejo, S. O., Yiase, S. G., Ahile, U. J., Tyohemba, T. G. & Gbertyo, J. A. (2013).
[10]. Inhibitory effect and adsorption parameters of extract of leaves of Portulaca oleracea of corrosion of aluminium in H2SO4 solution. Archives of Applied Science Research, **5**(1): 25-32
[11]. Dada, A. O., Olalekan, A. P., Olatunya, A. M., & Dada, O. (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rice Husk. Journal of Applied Chemistry, 3(1), 38-45.
[12]. Fadare, O. O., Okoronkwo, A. E. & Olasehinde, E. F. (2015). Assessment of Anti-Corrosion Potential of extract of Ficus Asperifolia-Miq (Moraceae) on mild steel in acid medium. African Journal of Pure and Applied Chemistry, **10**(1) 8-22.
[13]. Hofmann, A., Ratsch, C., & Shultes, R. (1992). Plants of Gods:Their Sacred, Heal- ing, and Hallucination Powers. USA: Healing Arts press.
[14]. Khadom, A. A. (2014). Effect of Temperature on Corrosion Inhibition of Copper- Nickel Alloy by Tetraethylenepentamine underflow Conditions. Journal of the Chilean Chemical Society, *59*(3), 2545-2549.
[15]. Stockburger, D. W. (n.d.). Multivariate Statistics: Concepts, Models, and Applicat-
[16]. ions: Multiple Regression with Many Predictor Variables. Retrieved January 02, 2017 fromhttp://www.psychstat.missouristate.edu/multibook/ mlt07.htm
[17]. Artificial Neural Network (n.d.). Basic Concepts. Retrieved January 02, 2017 from http://www.ele.ita.cta.br/~cairo/My_Publications/chap24.pdf
[18]. Fausett, L. (n.d.). Fundamentals of Neural Networks. Retrieved November 16, 2016 from www.csbdu.in/csbdu-old/pdf/fundamentals
[19]. Mean Squared Error and Residual Sum of Squares (2013). Cross Validation.
[20]. Retrieved September 20, 2016 from http://stats.stackexchange.com/ questions/73540/mean-squared-error-and-residual-sum-of-squares
[21]. Kriesel, D. (2005). A Brief Introduction to Neural Networks. Retrieved January 10, 2016 from http://www.dkriesel.com/_media/science/neuronalenetze-en-zeta2-2col-dkrieselcom.pdf
[22]. Mean Absolute Error (2016). The Mean Absolute Error. Retrieved September 19, 2016 from https://en.m.wikipedia.org/wiki/mean_absolute_error
[23]. Roberge, P. R. (2000): Corrosion Engineering (pp. 833-861). New York: McGraw-Hill.

Appendix 1: Prediction of corrosion inhibition of mild steel in sulphuric acid medium by thoroughly crushed leaves of Voacanga Africana.

Case	Time (h)	Conc_ Of_ H_2SO_4 (M)	Quantity _of_VA_ Crushed _Leaves (g)	Exp. Corrosion Rate, CR ($mgcm^{-2}h^{-1}$)	Prediction_by_MR		Prediction_by_ANN	
					CR	Error	CR	Error
1	1	0.7	0	8.1815	9.01291	-0.83141	8.1344	0.0471
2	2	0.7	0	7.5905	8.36924	-0.77874	6.8896	0.7009
3	3	0.7	0	7.1601	7.72558	-0.56548	5.8712	1.2889
4	4	0.7	0	6.3278	7.08192	-0.75412	5.0455	1.2823
5	5	0.7	0	6.5336	6.43826	0.09534	4.3784	2.1552
6	6	0.7	0	6.1291	5.79460	0.33450	3.8390	2.2901
7	7	0.7	0	5.7053	5.15094	0.55436	3.4011	2.3042
8	8	0.7	0	5.9448	4.50727	1.43753	3.0436	2.9012
9	1	0.7	15	1.6322	5.74639	-4.11419	2.3114	-0.6792
10	2	0.7	15	1.4464	5.10273	-3.65633	2.1727	-0.7263
11	3	0.7	15	0.7271	4.45907	-3.73197	2.0494	-1.3223
12	4	0.7	15	0.6346	3.81541	-3.18081	1.9394	-1.3048
13	5	0.7	15	0.6175	3.17175	-2.55425	1.8412	-1.2237
14	6	0.7	15	0.5872	2.52809	-1.94089	1.7533	-1.1661
15	7	0.7	15	0.8082	1.88442	-1.07622	1.6746	-0.8664
16	8	0.7	15	0.4433	1.24076	-0.79746	1.6043	-1.1610
17	1	0.7	30	2.4512	2.47988	-0.02868	1.5368	0.9144
18	2	0.7	30	1.3171	1.83622	-0.51912	1.4841	-0.1670
19	3	0.7	30	0.8432	1.19256	-0.34936	1.4364	-0.5932
20	4	0.7	30	0.5453	0.54890	-0.00360	1.3935	-0.8482
21	5	0.7	30	0.6111	-0.09476	0.70586	1.3550	-0.7439
22	6	0.7	30	0.5112	-0.73843	1.24963	1.3206	-0.8094
23	7	0.7	30	0.385	-1.38209	1.76709	1.2898	-0.9048
24	8	0.7	30	0.4393	-2.02575	2.46505	1.2624	-0.8231
25	1	0.7	45	1.6351	-0.78663	2.42173	1.2453	0.3898

26	2	0.7	45	1.3796	-1.43029	2.80989	1.2230	0.1566
27	3	0.7	45	0.782	-2.07395	2.85595	1.2032	-0.4212
28	4	0.7	45	0.7384	-2.71761	3.45601	1.1857	-0.4473
29	5	0.7	45	0.6668	-3.36128	4.02808	1.1701	-0.5033
30	6	0.7	45	0.5814	-4.00494	4.58634	1.1564	-0.5750
31	7	0.7	45	0.5137	-4.64860	5.1623	1.1443	-0.6306
32	8	0.7	45	0.4132	-5.29226	5.70546	1.1336	-0.7204
33	1	1.2	0	11.771	11.19837	0.57263	15.1098	-3.3388
34	2	1.2	0	11.976	10.55471	1.42129	13.0790	-1.1030
35	3	1.2	0	10.598	9.91105	0.68695	11.2475	-0.6495
36	4	1.2	0	9.4100	9.26739	0.14261	9.6508	-0.2408
37	5	1.2	0	8.9209	8.62372	0.29718	8.2950	0.6259
38	6	1.2	0	8.5939	7.98006	0.61384	7.1647	1.4292
39	7	1.2	0	8.0869	7.33640	0.75050	6.2330	1.8539
40	8	1.2	0	8.0791	6.69274	1.38636	5.4691	2.6100
41	1	1.2	15	3.2209	7.93186	-4.71096	3.5273	-0.3064
42	2	1.2	15	1.9982	7.28820	-5.29000	3.3048	-1.3066
43	3	1.2	15	1.2072	6.64454	-5.43734	3.1079	-1.9007
44	4	1.2	15	0.9642	6.00088	-5.03668	2.9315	-1.9673
45	5	1.2	15	0.9375	5.35721	-4.41971	2.7716	-1.8341
46	6	1.2	15	0.8679	4.71355	-3.84565	2.6252	-1.7573
47	7	1.2	15	0.7435	4.06989	-3.32639	2.4902	-1.7467
48	8	1.2	15	0.6821	3.42623	-2.74413	2.3649	-1.6828
49	1	1.2	30	2.9247	4.66535	-1.74065	2.2119	0.7128
50	2	1.2	30	2.078	4.02169	-1.94369	2.1174	-0.0394
51	3	1.2	30	0.9633	3.37803	-2.41473	2.0269	-1.0636
52	4	1.2	30	0.8314	2.73436	-1.90296	1.9409	-1.1095
53	5	1.2	30	0.894	2.09070	-1.19670	1.8596	-0.9656
54	6	1.2	30	0.653	1.44704	-0.79404	1.7832	-1.1302
55	7	1.2	30	0.7481	0.80338	-0.05528	1.7120	-0.9639
56	8	1.2	30	0.6313	0.15972	0.47158	1.6459	-1.0146
57	1	1.2	45	3.7117	1.39884	2.31286	1.6029	2.1088
58	2	1.2	45	1.1690	0.75518	0.41382	1.5461	-0.3771
59	3	1.2	45	1.2285	0.11151	1.11699	1.4940	-0.2655
60	4	1.2	45	0.986	-0.53215	1.51815	1.4466	-0.4606
61	5	1.2	45	0.5309	-1.17581	1.70671	1.4036	-0.8727
62	6	1.2	45	0.6627	-1.81947	2.48217	1.3648	-0.7021
63	7	1.2	45	0.5594	-2.46313	3.02253	1.3298	-0.7704
64	8	1.2	45	0.7072	-3.10680	3.81400	1.2985	-0.5913
65	1	2.2	0	35.3757	15.56930	19.8064	27.9350	7.4407
66	2	2.2	0	27.8496	14.92564	12.92396	26.6528	1.1968
67	3	2.2	0	23.8639	14.28198	9.58192	25.1330	-1.2691
68	4	2.2	0	20.5771	13.63832	6.93878	23.3835	-2.8064
69	5	2.2	0	19.423	12.99466	6.42834	21.4414	-2.0184
70	6	2.2	0	17.8311	12.35100	5.48010	19.3737	-1.5426
71	7	2.2	0	16.8414	11.70733	5.13407	17.2695	-0.4281
72	8	2.2	0	15.6365	11.06367	4.57283	15.2237	0.4128
73	1	2.2	15	9.1109	12.30279	-3.19189	6.9813	2.1296
74	2	2.2	15	6.5318	11.65913	-5.12733	6.3118	0.2200
75	3	2.2	15	5.5666	11.01547	-5.44887	5.7657	-0.1991
76	4	2.2	15	4.0363	10.37181	-6.33551	5.3197	-1.2834
77	5	2.2	15	3.9307	9.72815	-5.79745	4.9538	-1.0231
78	6	2.2	15	3.1686	9.08448	-5.91588	4.6518	-1.4832
79	7	2.2	15	2.7612	8.44082	-5.67962	4.4003	-1.6391
80	8	2.2	15	2.5634	7.79716	-5.23376	4.1886	-1.6252
81	1	2.2	30	8.2918	9.03628	-0.74448	3.6085	4.6833
82	2	2.2	30	4.5482	8.39262	-3.84442	3.5315	1.0167
83	3	2.2	30	3.7475	7.74896	-4.00146	3.4587	0.2888
84	4	2.2	30	2.5979	7.10530	-4.50740	3.3883	-0.7904
85	5	2.2	30	2.4884	6.46163	-3.97323	3.3190	-0.8306
86	6	2.2	30	1.8844	5.81797	-3.93357	3.2498	-1.3654
87	7	2.2	30	1.7833	5.17431	-3.39101	3.1797	-1.3964
88	8	2.2	30	1.7132	4.53065	-2.81745	3.1080	-1.3948
89	1	2.2	45	13.3512	5.76977	7.58143	3.0301	10.3211
90	2	2.2	45	4.9504	5.12611	-0.17571	2.9610	1.9894
91	3	2.2	45	3.8899	4.48245	-0.59255	2.8880	1.0019
92	4	2.2	45	2.8942	3.83878	-0.94458	2.8115	0.0827
93	5	2.2	45	3.1158	3.19512	-0.07932	2.7316	0.3842
94	6	2.2	45	2.4721	2.55146	-0.07936	2.6487	-0.1766
95	7	2.2	45	2.0575	1.90780	0.14970	2.5634	-0.5059
96	8	2.2	45	1.8577	1.26414	0.59356	2.4762	-0.6185