Corrosion Inhibition Model for Mild Steel in Sulphuric Acid by Crushed leaves of Clerodendrum Splendens (Verbenaceae)

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ABSTRACT

The use of thoroughly crushed fresh leaves of Clerodendrum Splendens to inhibit the corrosion of mild steel in 0.7M, 1.2M and 2.2M H_2SO_4 was studied using mass loss measurements. The corrosion rate curves decreased progressively with time. The addition of crushed leaves of Clerodendrum Splendens at 15g per litre of 0.7M H_2SO_4 gave the maximum inhibition efficiency of 87.58% with a corresponding corrosion rate reduction from $3.0524 mgcm^{-2}h^{-1}$ to $0.8288 mgcm^{-2}h^{-1}$. Artificial neural network and multiple regression were used to predict the experimental corrosion rate. 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. The activation energy, Q obtained for the uninhibited mild steel in 0.7M H_2SO_4 was 10,126.92J whereas in the presence of the crushed leaves of Clerodendrum Splendens at 15g per litre of 0.7M H_2SO_4, higher activation energy of 26,595. 38J was obtained, which suggests that greater energy needs to be attained before further corrosion can take place. The corrosion inhibition of mild steel in sulphuric acid solution by the crushed leaves of Clerodendrum Splendens was found to obey all the four examined adsorption isotherm models with the Langmuir isotherm maintaining the best fit of $R^2 = 1.000$; El-Awady isotherm, $R^2 = 0.876$; Temkin isotherm, $R^2 = 0.872$ and Freundlich isotherm, $R^2 = 0.853$. The FTIR spectrum of the adhered constituents of Clerodendrum Splendens' crushed leaves on the surface of the 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 and C≡C bonds.

Keywords: *Corrosion rate, Inhibition efficiency, Clerodendrum Splendens, Artificial neural network, Multiple regression, Adsorption isotherm models, Sulphuric acid.*

1. INTRODUCTION

Corrosion is the deterioration of the property of a material owing to its interaction with its environment (Kelly el al., 2003, p.1). Corrosion occurs when protective mechanisms have been overlooked, leaving the metal vulnerable to attack (Talbot and Talbot, 1998, p. 1). Metals in service often give a superficial impression of permanence, but all except gold are chemically unstable in air and air-saturated water at ambient temperatures and most are also unstable in air- free water. Almost all of the environments in which metals serve are potentially hostile and their successful use in engineering and commercial applications depends on protective mechanisms. In some metal/environment systems the metal is protected by passivity, a naturally formed surface condition inhibiting reaction. In other systems the metal surface remains active and some form of protection must be provided by design - this applies particularly to plain carbon and low-alloy irons and steels, which are the most prolific, least expensive, and most versatile metallic materials (Talbot and Talbot, 1998).

The addition of an inhibitor to a corrosive environment is one of the practical and cost effective methods of controlling metallic corrosion (Nnanna et al, 2016, p. 12); other methods of corrosion prevention being suitable design, appropriate materials selection, change of environment, cathodic protection, anodic protection and application of coatings (Bardal, 2003). The choice of any particular technique is usually based on economic considerations, but in many cases, aspects such as appearance, environment and safety must also be taken care of (Bardal, 2003).

Corrosion inhibitors are chemical compounds used in small concentrations to reduce the corrosion rate of metals and alloys in contact with any aggressive environment (Nnanna et al., 2016).

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Corrosion inhibitors may be inorganic or organic in nature. Considering inorganic inhibitors, the various simple chromate anions including chromate, CrO_4^{2-}, dichromate, $Cr_2O_7^{2-}$ and bichromate, $HCrO_4^-$ have all been reported to be potent corrosion inhibitors when they are present as soluble species in solution. Chromate is an effective inhibitor for Al, Fe, Mg, Cd, Sn and many other metals and alloys (Kelly et al., 2003). Recently, the mechanism of corrosion protection by soluble chromate inhibitors has been the subject of active research, which has attempted to understand and replicate its inhibiting functions with less toxic chemical substances (Kelly et al., 2003). According to (Al-Otaibi et al, 2014, p. 341) the popularity and use of synthetic compounds as a corrosion inhibitor is diminishing due to the strict environmental regulations and toxic effects of synthetic compounds on human or animal life. This development has instigated the search for green corrosion inhibitors as they are biodegradable, inexpensive and environmentally friendly (Nnnana et al., 2016).

In this study, we report the corrosion inhibition of mild steel in sulphuric acid by thoroughly crushed leaves of Clerodendrum Splendens. In essence, Clerodendrum Splendens is a woody or semi-woody evergreen vine or running shrub to *12ft (3.7m)* long that climbs by twining. The leaves are oval, to *7in (18cm)* long, and arranged in opposite pairs. The flowers of the plant are tuba shaped having a slender tube with an abruptly expanded corolla. They are scarlet (sometimes white), about *1in (2.5cm)* across and borne in dense terminal clusters to *5in (12.7cm)* inches long. Clerodendrum splendens prefers full sun, but does best with some shade during the hottest part of the day in summer. The flowers are extremely showy and attractive to butterflies as well as people (Clerodendrum Splendens, n.d.). The plant can be propagated from seed or from softwood cuttings in spring, or by breaking off pieces of root, or by removing rooted suckers. Branching and more extensive flowering can be encouraged by cutting the previous season's growth back to a suitable pair of buds. When this plant finds conditions that it likes, it can be difficult to contain, and can become rather invasive, putting up suckers from its roots all over the garden.

2. MATERIALS AND METHODS

2.1 Preparation of Coupons

Mild steel coupons of 4cm x 4cm dimensions were mechanically press-cut from a flat sheet metal of 0.15cm thickness with the composition: (wt %) C=0.20%, Zn=0.75%, Ti=0.28, Mn=0.23%, S=0.04%, P=0.035% and Fe balance. The coupons were first abraded with coarse and fine emery papers, treated with acetone and dried before figuring out their initial weights.

2.2 Preparation of Crushed Leaves

Fresh leaves of Clerodendrum Splendens were collected from the surrounding vegetation and thoroughly crushed with a manual blender. The crushed leaves were added at 15g per litre, 30g per litre and 45g per litre of 0.7M, 1.2M and 2.2M H_2SO_4. The moisture content of the fresh leaves of Clerodendrum Splendens was 70.17% as at the time the experiment was conducted.

2.3 Mass–loss Analysis

The initial weights of the mild steel coupons were measured with the ohaus electronic weighing balance (which gave results to the accuracy of 0.0001g) before immersion into different study environments. The mild steel coupons were immersed in 0.7M, 1.2M and 2.2M H_2SO_4 to which the crushed leaves of Clerodendrum Splendens had been added at 15g per litre, 30g per litre and 45g per litre of the aforementioned acid concentrations. Another experimental set-up wherein no inhibitor was added was prepared to provide comparison for results. The experimentation lasted for eight hours and in each hour; a coupon is removed from the system, cleaned and dried before the final weight is measured.

The corrosion rate was computed using the relationship (Ahmed, 2006, p. 58):

Corrosion Rate, $r_{corr} = w/(A.t)$ .... *(1)*
Where,
w = *weight loss in (mg).*
A = *exposed area in (cm^2).*
t = *time of exposure in (h).*

The corrosion inhibition efficiency was figured out by the formula:

I.E (%) = ((r_corr(a)-r_corr(b))/r_corr(a))*100 ... (2)

Where,

$r_{corr(a)}$ = *corrosion rate of the uninhibited system.*
$r_{corr(b)}$ = *corrosion rate of the inhibited system.*

2.4   Temperature Dependence

The Arrhenius equation is a formula for the temperature dependence of reaction rates. The equation was proposed by Svante Arrhenius in 1889, based on the work of Jacobus Henricus van't Hoff (Arrhenius Equation, 2016). Arrhenius equation has a vast application in determining the rate of chemical reactions and for the calculation of activation energy. Arrhenius argued that for reactants to transform into products, they must first acquire a minimum amount of energy, called the activation energy. According to (Del-Mondo et al., 2016), Arrhenius first measured the rate of a chemical reaction as a function of temperature according to the following equation:

$$K = Ae^{-Q/RT} \quad .... \quad (3)$$

If we take the natural logarithms of both sides of equation (3), we have:

$$InK = InA - Q/RT \quad .... \quad (4)$$

Where,
A=frequency factor or pre-exponential constant.
R=rate constant.
T=temperature.
Q=activation energy.

The Arrhenius equation is useful because it expresses a quantitative relationship between temperature, activation energy and rate constant. Perhaps, its most valuable use is in determining the activation energy of a reaction from rate experiments at different temperatures.

2.5   Development of Predictive Model
2.5.1   Multiple Regression Approach

Multiple regression helps in developing a predictive model by examining the relationship that exists between the dependent variable (the parameter to be predicted) and independent variables. In the context of the present study, the equation of the multiple regression for the prediction of the experimental corrosion rate, $mgcm^{-2}h^{-1}$ (i.e., the dependent variable) with respect to its relationship with some independent variables namely: time (h), concentration of acid (M) and quantity of crushed leaves (g) is given thus:

CR = b_o + C_1(time) + C_2(conc. of acid) + C_3(quantity of crushed leaves) ……….…… (5)

Where,
CR = corrosion rate.
b_o = *regression intercept.*
C_1 = *the change in CR for each 1 increment in time.*
C_2 = *the change in CR for each 1 increment in conc. of acid.*
C_3 = *the change in CR for each 1 increment in quantity of crushed leaves.*

2.5.2   Artificial Neural Network

A neural network is an interconnected assembly of simple processing elements, units or nodes, whose functionality is loosely based on the animal neuron. The processing ability of the network is stored in the inter-unit connection strengths, or weights, obtained by a process of adaptation to, or learning from, a set of training patterns (Gurney, 1997, p. 13).

The artificial equivalents of biological neurons are the nodes or units as shown in Figure 1. Synapses are modelled by a single number or weight so that each input is multiplied by a weight before being sent to the equivalent of the cell body. Here, the weighted signals are summed together by simple arithmetic addition to supply node activation. The activation is then compared with a threshold; if the activation exceeds the threshold, the unit produces a high-valued output (conventionally "1"), otherwise it outputs zero. A schematic representation of the artificial neural network model representing inputs

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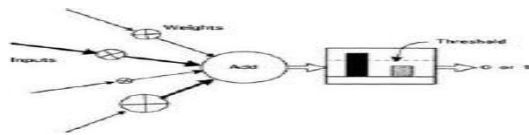and output for this present study is displayed in Figure 2.

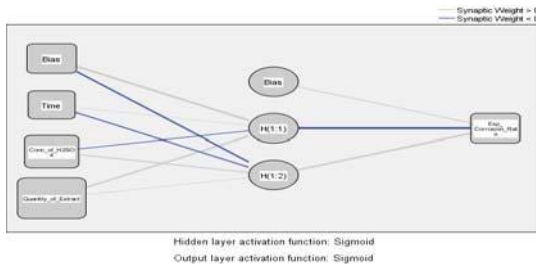Figure 1: Simple artificial neuron (Gurney, 1997, p. 14)

Figure 2: Artificial neural network model representing inputs and output for this present study

The net output can be computed by employing the relationship:

$$y_n = f(y_{input}) \quad .... \quad (6)$$

But,

$$y_{input} = a_p + \sum x_i w_{ip} \quad .... \quad (7)$$

$$f(x) = 1/(1+e^{-x}) \quad .... \quad (8)$$

Where,
y_{input} = *net input to* y_n.
f = activation function.
a_p = *bias of the unit.*

2.5.3 Error in Prediction

The inaccuracy in the prediction of any true outcome can be mathematically evaluated using the mean absolute error (MAE) or the mean squared error (MSE). Both MAE and MSE are computed by employing the formulae:

$$MAE = (1/N)\sum(a_i - b_i) \quad .... \quad (9)$$

$$MSE = (1/N)\sum(a_i - b_i)^2 \quad .... \quad (10)$$

Where,
a_i = *an estimator of parameter* b_i.
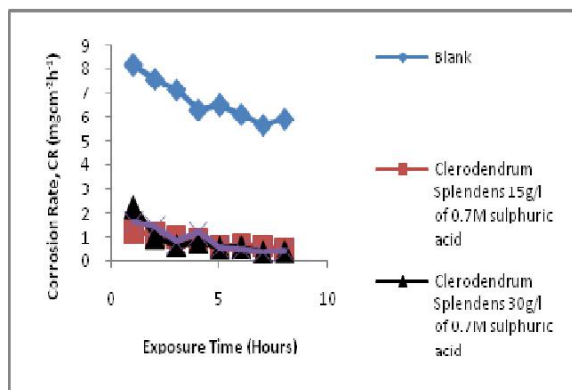*N = number of samples.*
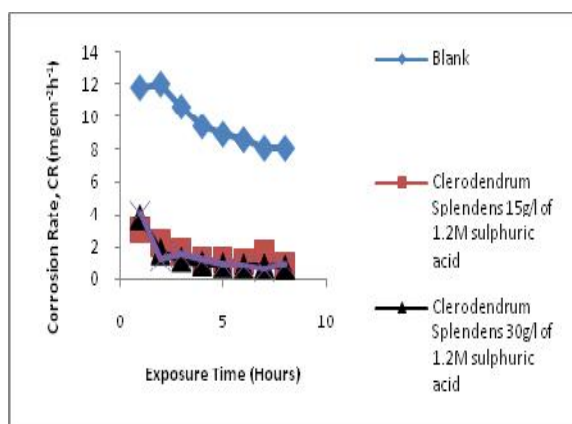b_i = *true value.*

3. RESULTS

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

t (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 Clerodendrum Splendens at 15g/l of H_2SO_4						
1	1.2576	84.63	3.0524	74.07	11.4169	67.73
2	1.1095	85.38	2.2131	81.52	7.0822	74.57
3	1.0262	85.67	1.6632	84.31	6.1552	74.21
4	0.8858	86.00	1.1813	87.45	5.3113	74.19
5	0.6308	90.35	1.1362	87.26	4.7457	75.57
6	0.7154	88.33	1.0470	87.82	3.8661	78.32
7	0.6535	88.55	1.5758	80.51	3.6727	78.19
8	0.4897	91.76	0.8288	89.74	3.3026	78.88
Av.	0.8461	87.58	1.5872	84.09	3.3026	78.88
Addition of crushed leaves of Clerodendrum Splendens at 30g/l of H_2SO_4						
1	2.3000	71.89	3.8134	67.60	11.0684	68.71
2	1.0644	85.98	1.6932	85.86	5.5676	80.01
3	0.6961	90.28	1.1782	88.88	4.4252	81.46
4	0.8488	86.59	0.9388	90.02	3.2456	84.23
5	0.5971	90.86	0.8550	90.42	2.8137	85.51
6	0.6390	89.57	0.7895	90.81	2.2300	87.49
7	0.4357	92.36	0.7817	90.33	1.9409	88.48
8	0.4545	92.35	0.7036	91.29	1.7491	88.81
Av.	0.8795	87.49	1.3442	86.90	4.1301	83.09
Addition of crushed leaves of Clerodendrum Splendens at 45g/l of H_2SO_4						
1	1.6700	79.59	4.0719	65.41	12.0355	65.98
2	1.4449	80.96	1.2590	89.49	6.6204	76.23
3	0.8403	88.26	1.5538	85.34	5.6053	76.51
4	1.1988	81.06	1.2467	86.75	2.8760	86.02
5	0.5693	91.29	0.9393	89.47	3.8296	80.28
6	0.5039	91.78	0.7992	90.70	3.6251	79.67
7	0.4000	92.99	0.6164	92.38	3.0126	82.11
8	0.4520	92.40	0.8829	89.07	2.7874	82.18
Av	0 8849	87 29	1 4212	86 08	5 0490	78 62

t = time of exposure in hours

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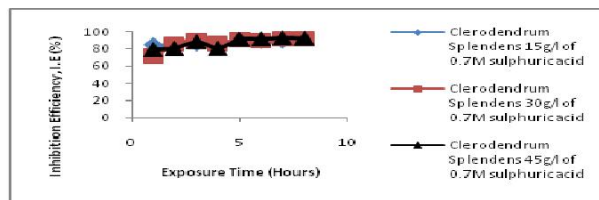**(a)**

(b)
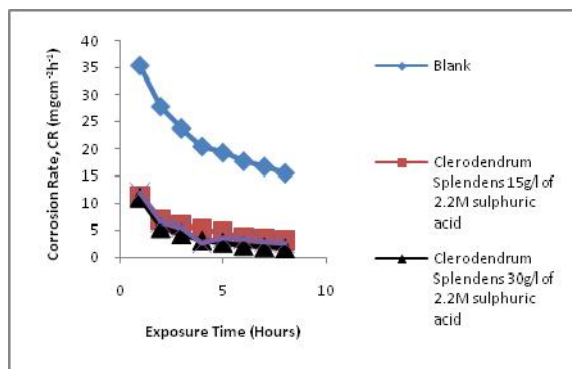
(c)

Figure 3: Effect of addition of thoroughly crushed leaves of Clerodendrum Splendens on corrosion of mild steel coupons immersed at:
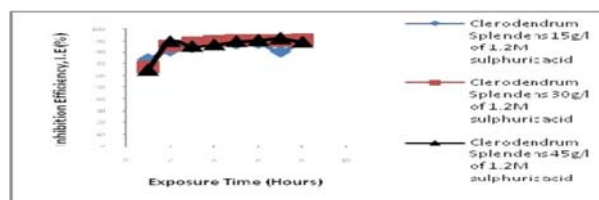(a) 15g/l, 30g/l and 45g/l of 0.7M H_2SO_4
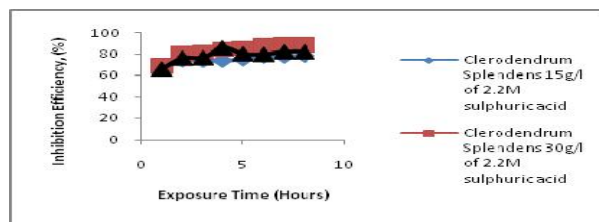(b) 15g/l, 30g/l and 45g/l of 1.2M H_2SO_4
(c) 15g/l, 30g/l and 45g/l of 2.2M H_2SO_4

(a)

(b)

(c)

Figure 4: Clerodendrum Splendens'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 crushed fresh leaves of Clerodendrum Splendens in sulphuric acid medium using multiple regression (MR)

	Model Coefficients			
	Constant	Time (h)	Conc. of Acids (M)	Quantity of Crushed Leaves (g)
H_2SO_4	6.246	-0.663	4.785	-0.212

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

Independent variable importance for the addition of crushed leaves of Clerodendrum Splendens into sulphuric acid medium

	Importance	Normalized Importance
Time	0.211	43.5%
Conc_of_H_2SO_4	0.303	62.3%
Quantity_of_Extract	0.486	100.0%

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**Parameter estimates for the addition of crushed leaves of Clerodendrum Splendens into sulphuric acid medium**

Predictor		Predicted		
		Hidden Layer 1		Output Layer
		H(1:1)	H(1:2)	Exp_Corrosion_Rate
Input Layer	(Bias)	3.535	-1.694	
	Time	0.009	-0.857	
	Conc_of_H2SO4	-0.367	1.005	
	Quantity_of_Extract	2.876	0.256	
Hidden Layer 1	(Bias)			0.780
	H(1:1)			-4.711
	H(1:2)			3.307

Table 4: Error analysis for the prediction of corrosion inhibition of mild steel by thoroughly crushed leaves of Clerodendrum Splendens 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	2.882664583	0.756030208
Mean Squared Error	15.96648831	1.265091087
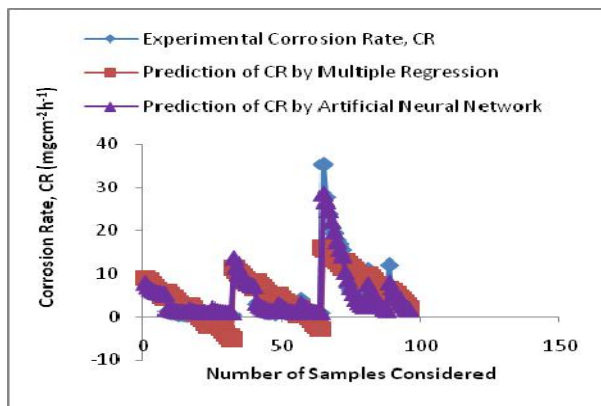
Figure 5: Comparison of error for the prediction of corrosion inhibition of mild steel by crushed leaves of Clerodendrum Splendens in sulphuric acid using multiple regression, MR and artificial neural network, ANN
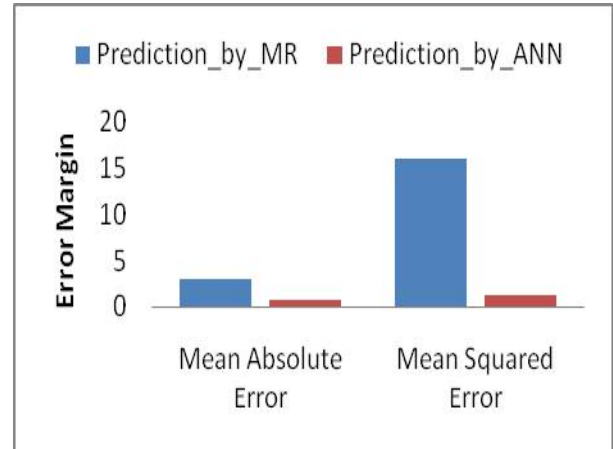
Figure 6: Error graph for the prediction of corrosion inhibition of mild steel by crushed leaves of Clerodendrum Splendens in sulphuric acid solution using multiple regression, MR and artificial neural network, ANN

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 Clerodendrum Splendens' fresh leaves

Temp (K)	$CR_{CS\ addition}$ ($mgcm^{-2}h^{-1}$)	CR_{Blank} ($mgcm^{-2}h^{-1}$)	Log $CR_{CS\ addition}$	Log CR_{Blank}	1/T (K^{-1})
298	0.8461	6.6966	-0.0726	0.8259	0.003356
318	5.2171	14.9549	0.7174	1.1748	0.003145
338	4.8370	13.6092	0.6846	1.1338	0.002959
358	6.0344	14.3791	0.7806	1.1577	0.002793

$Slope_{CS\ addition}$ = Slope for the addition of crushed leaves of Clerodendrum Splendens at 15g per litre of 0.7M acid concentration

$Slope_{Blank}$ = -528.9K^{-1} $Slope_{CS\ addition}$ = -1389K^{-1}

Q = 10,126.92J Q = 26,595.38J
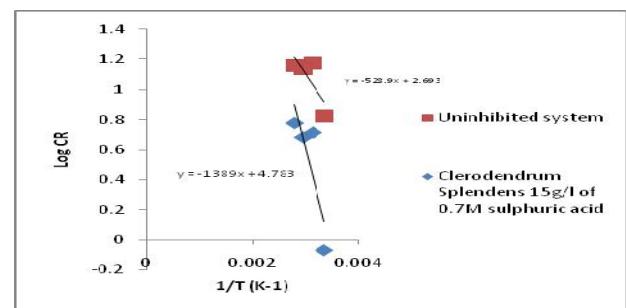
Figure 7: Arrhenius plot for the effect of addition of thoroughly crushed fresh leaves of Clerodendrum Splendens to sulphuric acid induced corrosion of mild steel coupons immersed at 15g per litre of 0.7M H_2SO_4

Table 6: Calculated parameters of four adsorption isotherm models for adsorption of crushed fresh leaves of Clerodendrum Splendens 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
1.147	1.000	-0.002	0.853	-0.002	0.873	-0.022	0.876
Parameters							
C (g)	Log C	In C	Θ	C/ Θ	Log Θ	1- Θ	Log (Θ/1-Θ)
15	1.1761	2.7081	0.8753	17.1272	-0.0576	0.1242	0.8483
30	1.4771	3.4012	0.8749	34.2896	-0.0580	0.1251	0.8447
45	1.6532	3.8067	0.8729	51.5523	-0.0590	0.1271	0.8368

(a)　　　　　　　　　(b)

(c)　　　　　　　　　(d)

Figure 8: Adsorption Isotherm models for adsorption of the crushed leaves of Clerodendrum Splendens on the mild steel surface in sulphuric acid medium: (a) Langmuir adsorption isotherm (b) Freundlich adsorption isotherm (c) Temkin adsorption isotherm (d) El-Awady adsorption isotherm

Figure 9: FTIR Spectrum of film on mild steel surface after immersion for eight hours in a medium containing

crushed fresh leaves of Clerodendrum Splendens at 30g per litre of 0.7M H₂SO₄

(a)

(a)　　　　　　　　　(b)

Figure 10: SEM characteristics of: (a) the mild steel used for the experiment (b) the blank solution of 0.7M H₂SO₄ (c) the presence of thoroughly crushed leaves of Clerodendrum Splendens at 30g per litre of 0.7M H₂SO₄

4. DICUSSION OF RESULTS

4.1 Effect of Addition of thoroughly Crushed Leaves of Clerodendrum Splendens on the Corrosion of Mild Steel Coupons Immersed in Sulphuric Acid Solution
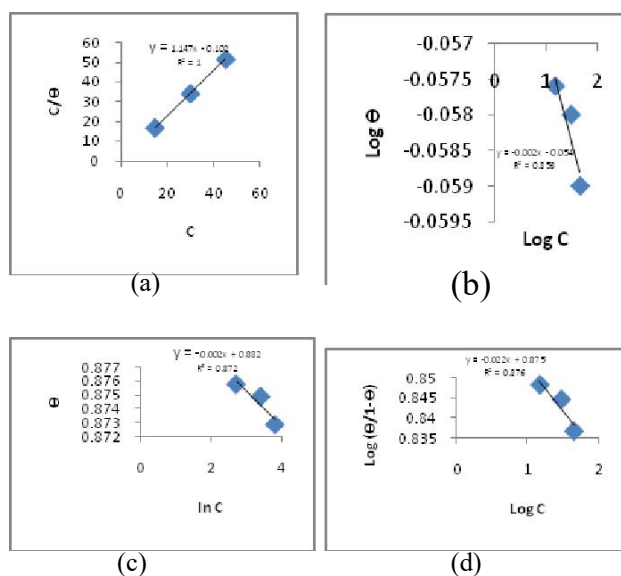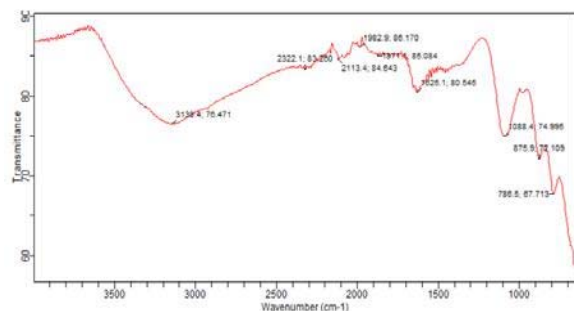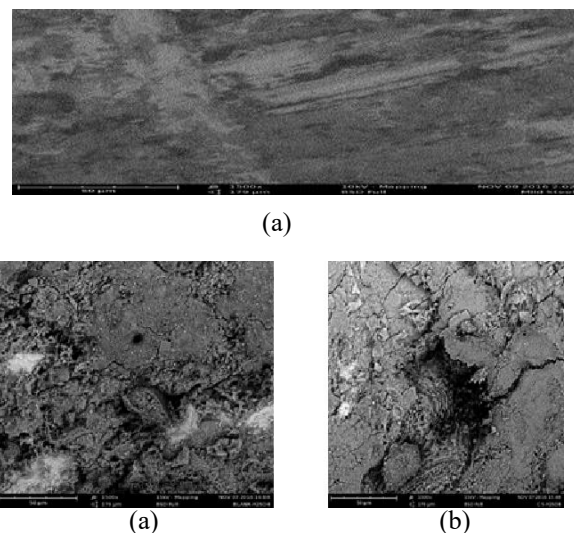
By adding the crushed leaves of Clerodendrum Splendens at 15g per litre of 0.7M, 1.2M and 2.2M acid concentrations the following average corrosion rate, CR and inhibition efficiency, I.E in the order CR (I.E) were obtained as presented in Table 1: $0.8461 mgcm^{-2}h^{-1}$ (87.58) in 0.7M H₂SO₄; $1.5872 mgcm^{-2}h^{-1}$ (84.09%) in 1.2M H₂SO₄ and $3.3026 mgcm^{-2}h^{-1}$ (78.88%) in 2.2M H₂SO₄. As the addition of the crushed leaves was increased to 30g per litre of various acid concentrations, the corresponding average corrosion rate and inhibition efficiency were: $0.8795 mgcm^{-2}h^{-1}$ (87.49%) in 0.7M H₂SO₄; $1.3442 mgcm^{-2}h^{-1}$ (86.90%) in 1.2M H₂SO₄ and $4.1301 mgcm^{-2}h^{-1}$ (83.09%) in 2.2M H₂SO₄. Further addition of the crushed leaves of Clerodendrum Splendens at 45g per litre of different acid concentrations gave the following average

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corrosion rate and inhibition efficiency: $0.8849 mgcm^{-2}h^{-1}$ (87.29%) in 0.7M H_2SO_4; $1.4212 mgcm^{-2}h^{-1}$ (86.08%) in 1.2M H_2SO_4 and $5.0490 mgcm^{-2}h^{-1}$ (78.62%) in 2.2M H_2SO_4.

In the entire study environment, the corrosion rate did not just increase with increase in acid concentration but was observed to be lower in the presence of the crushed leaves of Clerodendrum Splendens than in the blank sulphuric acid solution as shown in Figure 3.

The inhibition efficiency–time curves for mild steel coupons occasioned by the addition of the thoroughly crushed leaves of Clerodendrum Splendens at 15g per litre, 30g per litre and 45g per litre of 0.7M, 1.2M and 2.2M H_2SO_4 are displayed in Figure 4. The inhibition efficiency curves increased with increase in exposure time. The maximum inhibition efficiency of 87.58% was achieved by the addition of the crushed leaves of Clerodendrum Splendens at 15g per litre of 0.7M H_2SO_4.

4.2 Prediction of Corrosion Inhibition of Mild Steel in Sulphuric Acid by the Crushed Leaves of Clerodendrum Splendens

The experimental corrosion rates of mild steel coupons with and without the addition of crushed leaves of Clerodendrum Splendens to sulphuric acid medium were predicted by multiple regression and artificial neural network. The predicted values are presented in Appendix 1.

Using multiple regression as illustrated in Table 2, the predictive equation for the addition of thoroughly crushed leaves of Clerodendrum Splendens to sulphuric acid solution is given thus:

$CR_{CS\ in\ H2SO4\ by\ MR}$ = 6.246 - 0.663(time) + 4.785(conc. of acid) - 0.212(quantity of crushed leaves) ……. (11)

The prediction of the experimental corrosion rate by the artificial neural network revealed the importance of independent variables; (time (h), concentration of acid (M) and quantity of extract (g)) in the prediction of the dependent variable (Corrosion rate, CR ($mgcm^{-2}h^{-1}$) for the addition of thoroughly crushed leaves of Clerodendrum Splendens to sulphuric acid solution as presented in Table 3.

The quantity of the crushed leaves of Clerodendrum Splendens greatly influenced the prediction of the experimental corrosion rate by 48.6%, followed by concentration of acid, 30.3% and lastly the time of exposure, 21.1%.

The mean absolute error (MAE) and mean squared error (MSE) were employed to investigate how close the predicted corrosion rate was to the observed corrosion rate. The comparison of error results for the prediction of corrosion inhibition of mild steel in sulphuric acid by the crushed leaves of Clerodendrum Splendens using multiple regression and artificial neural network is 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 on Corrosion of Mild Steel in H_2SO_4

The results of the variation in temperature between 298K and 358K on the corrosion of mild steel without and with the addition of crushed leaves of Clerodendrum Splendens at 15g per litre of 0.7M H_2SO_4 are presented in Table 5 and shown in Figure 7. The activation energy, Q obtained for the uninhibited mild steel in 0.7M H_2SO_4 was 10,126.92J whereas in the presence of the inhibitor at 15g per litre of 0.7M H_2SO_4, higher activation energy of 26,595.38J was obtained. The higher value of activation energy obtained by the introduction of thoroughly crushed leaves of Clerodendrum Splendens to the corrodent suggests that greater energy needs to be attained before further corrosion can take place.

4.4 Adsorption Isotherm

The corrosion inhibition of mild steel in sulphuric acid by the crushed leaves of Clerodendrum Splendens was found to obey four adsorption isothem models namely: Langmuir isotherm, R^2 = 1.000; El-Awady isotherm, R^2 = 0.876; Temkin isotherm, R^2 = 0.872 and Freundlich isotherm, R^2 = 0.853. Adsorption from solution in most cases, leads to the formation of a layer of single molecule thickness on the surface of the solid.

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This type of adsorption is also affected by temperature and concentration (Sharma and Sharma, 2005). The equations of the aforementioned adsorption isotherms are given below:

Langmuir: Conc/Ө = Conc + 1/K$_r$ .... **(12)**
Freundlich: LogӨ = LogKr + nLogConc .... **(13)**
El-Awady: Log(Ө/1-Ө) = LogK$_r$ + yLogConc .. **(14)**
Temkin: Ө = bInA + bInConc .... **(15)**

Where,
Ө = the portion of surface coverage.
Conc = the concentration of the inhibitor.
K$_r$ = the equilibrium constant for the adsorption/desorption process.
b = Constant related to heat of sorption (J/mol).

4.5   FTIR Analysis

The FTIR spectrum of the adhered constituents of thoroughly crushed leaves of Clerodendrum Splendens 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 band at $2113.4 cm^{-1}$ indicates the presence of C≡C stretching of alkynes. The double carbon-carbon stretching of alkenes is spotted around $1625.1 cm^{-1}$. The conjugated alkenes appear around $1600 cm^{-1}$ whereas non-conjugated alkenes are found within the frequency, $1660 cm^{-1}$.

4.6 SEM Micrograph for the Corrosion Inhibition of Mild Steel in H_2SO_4 by Crushed Leaves of Clerodendrum Splendens

The SEM image of the mild steel coupon that was used for this present research is shown in Figure 10(a). The corrosion of mild steel in a blank solution of 0.7M H_2SO_4 shows that degradation is localized and does not take place uniformly over the surface of the steel (Figure 10(b)). The mild steel's surface was somewhat protected by the addition of thoroughly crushed leaves of Clerodendrum Splendens at 30g per litre of 0.7M H_2SO_4 although localized degradation is observed near the centre of the image as displayed in Figure 10(c). This development may have been caused by insufficient addition of the crushed plant-leaves.

5.   CONCLUSION

1.   The comparison of error results shows 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.

2.   The corrosion inhibition of mild steel in H_2SO_4 by the crushed leaves of Clerodendrum Splendens was found to obey four adsorption isotherm models namely: Langmuir isotherm, R^2 = 1.000; El-Awady isotherm, R^2 = 0.876, Temkin isotherm, R^2 = 0.872 and Freundlich isotherm, R^2 = 0.853.

3.   The FTIR spectrum of the adhered constituents of thoroughly crushed leaves of Clerodendrum Splendens on the surface of mild steel coupon immersed at 30g per litre of 0.7M H_2SO_4 for eight hours indicates the stretching vibrations of C≡C and C=C bonds.

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Appendix 1: Prediction of Corrosion Inhibition of Mild Steel in Sulphuric Acid Medium by thoroughly Crushed Leaves of Clerodendrum Splendens

Case	t (h)	Conc_Of_H₂SO₄ (M)	Quantity_of_CS_Crushed_Leaves (g)	Exp. Corrosion Rate, CR (mgcm⁻²h⁻¹)	Prediction_by_MR CR	Error	Prediction_by_ANN CR	Error
1	1	0.7	0	8.1815	8.9322	-0.7507	7.9833	0.1982
2	2	0.7	0	7.5905	8.2688	-0.6783	7.1099	0.4806
3	3	0.7	0	7.1601	7.6054	-0.4453	6.4987	0.6614
4	4	0.7	0	6.3278	6.9420	-0.6142	6.0729	0.2549
5	5	0.7	0	6.5336	6.2786	0.2550	5.7757	0.7579
6	6	0.7	0	6.1291	5.6152	0.5139	5.5667	0.5624
7	7	0.7	0	5.7053	4.9518	0.7535	5.4180	0.2873
8	8	0.7	0	5.9448	4.2884	1.6564	5.3107	0.6341
9	1	0.7	15	1.2576	5.7535	-4.4959	2.0520	-0.7944
10	2	0.7	15	1.1095	5.0901	-3.9806	1.7946	-0.6851
11	3	0.7	15	1.0262	4.4267	-3.4005	1.6229	-0.5967
12	4	0.7	15	0.8858	3.7633	-2.8775	1.5079	-0.6221
13	5	0.7	15	0.6308	3.0999	-2.4691	1.4305	-0.7997
14	6	0.7	15	0.7154	2.4365	-1.7211	1.3780	-0.6626
15	7	0.7	15	0.6535	1.7731	-1.1196	1.3422	-0.6887
16	8	0.7	15	0.4897	1.1097	-0.6200	1.3175	-0.8278
17	1	0.7	30	2.3000	2.5748	-0.2748	1.8470	0.4530
18	2	0.7	30	1.0644	1.9114	-0.8470	1.5901	-0.5257
19	3	0.7	30	0.6961	1.2480	-0.5519	1.4193	-0.7232
20	4	0.7	30	0.8488	0.5846	0.2642	1.3057	-0.4569
21	5	0.7	30	0.5971	-0.0788	0.6759	1.2297	-0.6326
22	6	0.7	30	0.6390	-0.7422	1.3812	1.1786	-0.5396
23	7	0.7	30	0.4357	-1.4056	1.8413	1.1440	-0.7083
24	8	0.7	30	0.4545	-2.0690	2.5235	1.1205	-0.6660
25	1	0.7	45	1.6700	-0.6039	2.2739	2.0234	-0.3534
26	2	0.7	45	1.4449	-1.2673	2.7122	1.7029	-0.2580
27	3	0.7	45	0.8403	-1.9307	2.7710	1.4892	-0.6489
28	4	0.7	45	1.1988	-2.5941	3.7929	1.3472	-0.1484
29	5	0.7	45	0.5693	-3.2575	3.8268	1.2526	-0.6833
30	6	0.7	45	0.5039	-3.9209	4.4248	1.1892	-0.6853
31	7	0.7	45	0.4000	-4.5843	4.9843	1.1465	-0.7465
32	8	0.7	45	0.4520	-5.2477	5.6997	1.1176	-0.6656
33	1	1.2	0	11.7710	11.3247	0.4463	13.7145	-1.9435
34	2	1.2	0	11.976	10.6613	1.3147	11.762	0.2140
35	3	1.2	0	10.598	9.9979	0.6001	10.2757	0.3223
36	4	1.2	0	9.4100	9.3345	0.0755	9.1920	0.2180
37	5	1.2	0	8.9209	8.6711	0.2498	8.4204	0.5005
38	6	1.2	0	8.5939	8.0077	0.5862	7.8766	0.7173
39	7	1.2	0	8.0869	7.3443	0.7426	7.4941	0.5928
40	8	1.2	0	8.0791	6.6809	1.3982	7.2238	0.8553
41	1	1.2	15	3.0524	8.1460	-5.0936	3.3087	-0.2563
42	2	1.2	15	2.2131	7.4826	-5.2695	2.6708	-0.4577
43	3	1.2	15	1.6632	6.8192	-5.1560	2.2350	-0.5718
44	4	1.2	15	1.1813	6.1558	-4.9745	1.9426	-0.7613
45	5	1.2	15	1.1362	5.4924	-4.3562	1.7474	-0.6112
46	6	1.2	15	1.0470	4.8290	-3.7820	1.6166	-0.5696
47	7	1.2	15	1.5758	4.1656	-2.5898	1.5285	0.0473
48	8	1.2	15	0.8288	3.5022	-2.6734	1.4687	-0.6399
49	1	1.2	30	3.8134	4.9673	-1.1539	2.8873	0.9261
50	2	1.2	30	1.6932	4.3039	-2.6107	2.3008	-0.6076
51	3	1.2	30	1.1782	3.6405	-2.4623	1.8964	-0.7182
52	4	1.2	30	0.9388	2.9771	-2.0383	1.6248	-0.6860
53	5	1.2	30	0.855	2.3137	-1.4587	1.4441	-0.5891
54	6	1.2	30	0.7895	1.6503	-0.8608	1.3240	-0.5345
55	7	1.2	30	0.7817	0.9869	-0.2052	1.2437	-0.462
56	8	1.2	30	0.7036	0.3235	0.3801	1.1897	-0.4861
57	1	1.2	45	4.0719	1.7886	2.2833	3.2651	0.8068
58	2	1.2	45	1.2590	1.1252	0.1338	2.5661	-1.3071
59	3	1.2	45	1.5538	0.4618	1.0920	2.0717	-0.5179
60	4	1.2	45	1.2467	-0.2016	1.4483	1.7355	-0.4888
61	5	1.2	45	0.9393	-0.8650	1.8043	1.5110	-0.5717
62	6	1.2	45	0.7992	-1.5284	2.3276	1.3618	-0.5626
63	7	1.2	45	0.6164	-2.1918	2.8082	1.2625	-0.6461

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64	8	1.2	45	0.8829	-2.8552	3.7381	1.1960	-0.3131
65	1	2.2	0	35.3757	16.1097	19.266	28.5406	6.8351
66	2	2.2	0	27.8496	15.4463	12.403	26.8044	1.0452
67	3	2.2	0	23.8639	14.7829	9.0810	24.6445	-0.7806
68	4	2.2	0	20.5771	14.1195	6.4576	22.2126	-1.6355
69	5	2.2	0	19.423	13.4561	5.9669	19.7639	-0.3409
70	6	2.2	0	17.8311	12.7927	5.0384	17.5480	0.2831
71	7	2.2	0	16.8414	12.1293	4.7121	15.7119	1.1295
72	8	2.2	0	15.6365	11.4659	4.1706	14.2855	1.3510
73	1	2.2	15	11.4169	12.9310	-1.5141	10.4802	0.9367
74	2	2.2	15	7.0822	12.2676	-5.1854	8.6704	-1.5882
75	3	2.2	15	6.1552	11.6042	-5.4490	6.9355	-0.7803
76	4	2.2	15	5.3113	10.9408	-5.6295	5.4402	-0.1289
77	5	2.2	15	4.7457	10.2774	-5.5317	4.2687	0.4770
78	6	2.2	15	3.8661	9.6140	-5.7479	3.4158	0.4503
79	7	2.2	15	3.6727	8.9506	-5.2779	2.8238	0.8489
80	8	2.2	15	3.3026	8.2872	-4.9846	2.4229	0.8797
81	1	2.2	30	11.0684	9.7523	1.3161	7.6777	3.3907
82	2	2.2	30	5.5676	9.0889	-3.5213	6.3778	-0.8102
83	3	2.2	30	4.4252	8.4255	-4.0003	5.1130	-0.6878
84	4	2.2	30	3.2456	7.7621	-4.5165	4.0031	-0.7575
85	5	2.2	30	2.8137	7.0987	-4.2850	3.1192	-0.3055
86	6	2.2	30	2.2300	6.4353	-4.2053	2.4689	-0.2389
87	7	2.2	30	1.9409	5.7719	-3.8310	2.0159	-0.0750
88	8	2.2	30	1.7491	5.1085	-3.3594	1.7101	0.0390
89	1	2.2	45	12.0355	6.5736	5.4619	8.0993	3.9362
90	2	2.2	45	6.6204	5.9102	0.7102	6.8785	-0.2581
91	3	2.2	45	5.6053	5.2468	0.3585	5.6221	-0.0168
92	4	2.2	45	2.876	4.5834	-1.7074	4.4530	-1.5770
93	5	2.2	45	3.8296	3.9200	-0.0904	3.4707	0.3589
94	6	2.2	45	3.6251	3.2566	0.3685	2.7167	0.9084
95	7	2.2	45	3.0126	2.5932	0.4194	2.1766	0.8360
96	8	2.2	45	2.7874	1.9298	0.8576	1.8065	0.9809

t = time of exposure (hours)