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Modelling of Corrosion Inhibition of Mild Steel in Hydrochloric Acid by Crushed Leaves of Sida Acuta (Malvaceae)

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 corrosion inhibition of mild steel in 0.7M, 1.2M and 2.2M HCl by thoroughly pounded fresh leaves of Sida Acuta has been investigated using the weight-loss method. Corrosion rate curves progressively decreased with time. The maximum inhibition efficiency of 71.16% was attained when the crushed leaves of Sida Acuta were added at 15g per litre of 0.7M HCl whilst the corrosion rate reduced from 1.0485 to 0.3006mgcm^{-2}h^{-1}. The predictive corrosion rate model was developed using multiple regression and artificial neural network. Predictions of the experimental corrosion rate values 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}). The time of exposure immensely contributed to the prediction of the experimental corrosion rate by 48.9%, followed by the quantity of crushed leaves, 26.2% and finally the concentration of acid, 25.0%. Predictions by the artificial neural network gave minimal errors and were closer to the experimental corrosion rate values in comparison with the predictions by multiple regression. The protective film formed on the mild steel surface was analysed by FTIR spectroscopy and surface electron microscopy (SEM). The FTIR analysis revealed that the adsorbed constituents of the pounded fresh leaves of Sida Acuta on the surface of mild steel were associated with the stretching vibrations of C≡C, C=C, C=O and O–H bonds. The SEM image shows that the degradation of the surface of mild steel in an uninhibited solution of 0.7M HCl is localized but the addition of the inhibitor remarkably prevented the surface of mild steel from corrosion. Four adsorption isotherm models were tested and the results show that the corrosion inhibition of mild steel by the crushed fresh leaves of Sida Acuta in hydrochloric acid obeys all the isotherm models with the Langmuir adsorption isotherm maintaining the best fit of R^2 = 0.996; El-Awady, R^2 = 0.961; Temkin, R^2 = 0.952 and Freundlich, R^2 = 0.942. The phytochemical analysis of Sida Acuta's leaves disclosed the presence of alkanoid, tannin, saponin, phytate, flavonoid and phenol.

Keywords: *Corrosion rate; Inhibition efficiency; Sida Acuta; Crushed fresh leaves; FTIR analysis; SEM image; Multiple regression; Artificial neural network*

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I. INTRODUCTION

Corrosion is an unwanted oxidation of a metal. It cuts short the lifetime of steel products such as bridges and automobiles; replacing corroded metal parts costs billions of dollars a year. Corrosion is an electrochemical process, and the electrochemical series gives us insight into why corrosion occurs and how it can be prevented (Jones and Atkins, 2000, p.821). Corrosion inhibition is a veritable measure that is employed to combat corrosion. A substance that is able to prevent the corrosion of any metal or alloy when added in minute quantity to the corrodent is an inhibitor. Corrosion inhibitors are added to a corrosion system to decrease or eliminate anodic dissolution; a good example of their application is in acid pickling operations that are employed to remove oxide scales formed during metal working operations (Anyakwo, 2007, p. 8). All the same, an inhibitor hinders corrosion reactions either by reducing the probability of corrosion occurrence or by reducing the rate of attack or both (Raja and Sethuraman, 2008).

The toxic nature of the known effective inhibitors that are chromate and arsenate-based has led to the study of various alternative means of corrosion inhibition. Plant-leaf extracts have shown promise in inhibiting the corrosion of mild steel in acidic medium. According to (Patni et al., 2013), plant extracts contain many organic compounds that have polar atoms such as O, P, S and N which adsorb on the metal surface to form protective films. However, the corrosion inhibition of mild steel by thoroughly crushed fresh leaves of Sida Acuta is relevant to this present study.

Sida Acuta is a small, erect, perennial shrub, branching profusely from the base. It usually ranges from 30-150cm in height, but grows to 3m in favourable conditions in northern Australia (Lonsdale et al., 1995). The stems are almost woody, with a tough stringy bark. There is a deep, tough taproot. The leaves are alternate, lanceolate, acute, tapering towards both ends, and on a short, hairy petiole 3-6mm long. The leaves have toothed margins, smooth or sparse stellate hairs and prominent veins on the under surface. The leaves are quite variable in size, from 2-9cm long and 0.5-4cm wide. The pair of stipules at the base of each leaf is not equal, with one frequently much narrower than the other. Sida Acuta is found on most soil types, except seasonally flooded clays or soils derived from limestone (Rojas-Sandoval et al., 2009). It competes vigorously with other plant species, but does best in tropical or sub-tropical regions with a distinct wet and dry season. It has a deep taproot and can withstand drought, mowing and shallow tillage. It is a weed of degraded pastures, tree plantations, cereals, root crops, vegetables, planted forests, lawns, roadsides, and waste places (Pitt, 1992; Flanagan et al., 2000). In habitats where it occurs, it tends to flourish in riparian areas near watercourses. It has been reported at up to 1500m altitude in Indonesia, at medium and higher elevations in Kenya and in the foothills of the Andes in Peru (Rojas-Sandoval et al., 2009).

Investigation of Sida Acuta (wireweed) plant extract as corrosion inhibitor for aluminium-copper-magnesium alloy in acidic medium was carried out by (Ayeni et al., 2014, p. 286). They reported that the presence of Sida Acuta plant extract reduced corrosion rate from 0.0012 to 0.0001mpy and percentage protection increased from 37.42% to 93.63% within a ten-day period with increase in percentage volume of the extract.

Further analysis of the surface of mild steel with and without the presence of an inhibitor can be done using Fourier Transform infrared (FTIR) Spectrometer and Scanning Electron Microscope (SEM). The FTIR spectrometer is used to figure out the type of bonding, particularly functional groups present in organic compounds. It is useful in predicting whether organic inhibitors are adsorbed or not on the metal surface. On the other hand, the SEM produces black and white, three-dimensional images. Image magnification can be up to 10 nanometres and the intense interactions that take place on the surface of the specimen provide a greater depth of view, higher-resolution and ultimately, a more detailed surface picture (Scanning Electron Microscopy, 2016).

In corrosion inhibition study, a predictive model presents a well-informed relationship between the acid induced corrosion and the rate of corrosion after the addition of an inhibitor. Mathematical models are designed to describe physical systems by equations or, more in general, by logical and computational structures (Bellomo et al., 2007). However, system modelling and simulation of the actual physical system offer a better alternative in situations where research facilities are in short supply and in some cases non–existent (Okoro, 2008). Multiple regression is an extension of simple linear regression. It is used when we want to predict the value of a variable, based on the value of two or more other variables. (Lærd, 2013, para. 1).

II. MATERIALS AND METHODS

2.1 Fabrication of mild steel coupons

Mild steel coupons of *40mm x 40mm x 1.5mm* dimensions were cut from a sheet metal with the following composition (wt %) C=0.20%, Zn=0.75%, Ti=0.28, Mn=0.23%, S=0.04%, P=0.035% and Fe balance. The initial weight of each specimen was measured using the Ohaus electronic weighing balance before immersion.

2.2 Weight–loss experimentation

Sida Acuta's leaves, obtained within the immediate vicinity of the Federal University of Technology, Owerri were thoroughly pounded and added to the hydrochloric acid solution at 15g per litre, 30g per litre and 45g per litre of 0.7M, 1.2M and 2.2M HCl. The acid concentration was prepared using dilution formula. Meanwhile, a different experimental set-up was prepared wherein no inhibitor was added in order to serve the purpose of comparison. Each experiment lasted for eight hours. In addition, the moisture content of the fresh-leaves of Sida Acuta was about 64.77% as at the time of the experiment was conducted.

The corrosion rate, CR was calculated by using the formula (Fadare et al., 2016):

$$CR = \frac{w}{A.t} \quad \ldots \quad (1)$$

Where,

w = weight loss in g.

A = exposed area in cm^{-2}*.*

t = exposure time in hours.

The corrosion inhibition efficiency was obtained by the relationship:

$$\text{Inhibition Efficiency, I.E (\%)} = ((CR_{un} - CR_{in})/CR_{un}) \times 100 \quad \ldots \quad (2)$$

Where,

CR_{un} *= Corrosion Rate of the uninhibited system.*

CR_{in} *= Corrosion Rate of the inhibited system.*

2.3 Analysis of experimental data

2.3.1 Multiple regression (MR)

Regression analysis is a statistical tool for the investigation of relationships between variables (Sykes, 1992). According to (Lærd Statistics, 2013), multiple regression is an extension of simple linear regression. It is used when we want to predict the value of a variable based on the value of two or more other variables. The variable we want to predict is called the dependent variable (or sometimes, the outcome, target or criterion variable). The variables we are using to predict the value of the dependent variable are called the independent variables (or sometimes, the predictor, explanatory or regressor variables).

The formula for multiple regression is stated thus (Higgins, 2005):

$$Y^{*} = a + b_1X_1 + b_2X_2 + \cdots + b_nX_n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where,

Y^*= the predicted value of Y (which is the dependent variable).

a = the 'Y intercept'.

b_1 = the change in Y for each 1 increment change in X_1.

b_2 = the change in Y for each 1 increment change in X_2.

X_1 = an X score on your first independent variable for which you are trying to predict a value of Y.

X_2 = an X score on your second independent variable for which you are trying to predict a value of Y.

2.3.2 Artificial neural network

Artificial neural networks (ANNs) are computer models inspired by the structure of biological neural networks. They consist of highly interconnected nodes, and their overall ability to help predict outcomes is determined by the connections between these neurons (Ayer et al., 2010, p. 15). ANNs are capable of 'learning', that is, they use experience to improve their performance. When exposed to a sufficient number of samples, ANNs can generalise to others they have not yet encountered.

An artificial neural network consists of a number of very simple and highly interconnected processors, also called neurons, which are analogous to the biological neurons in the brain. The neurons are connected by weighted links passing signals from one neuron to another. Each neuron receives a number of input signals through its connections; however, it never produces more than a single output signal. The output signal is transmitted through the neuron's outgoing connection (corresponding to the biological axon). The outgoing connection, in turn, splits into a number of branches that transmit the same signal (the signal is not divided among these branches in any way). The outgoing branches terminate at the incoming connections of other neurons in the network. A schematic representation of artificial neural network model representing inputs and output for this present study is displayed in Figure 1.

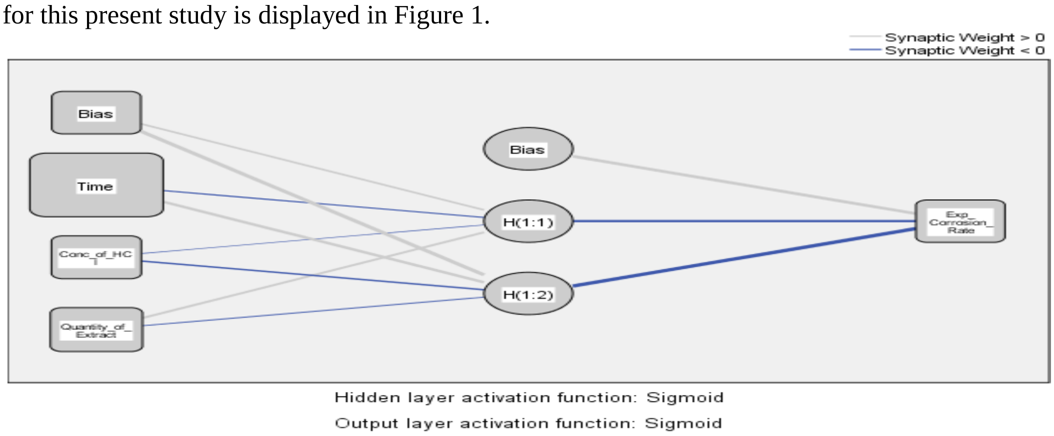


Figure 1: Schematic representation of artificial neural network model representing inputs and output.

Given a unit, j in a hidden or output layer, the net input, I_j, to unit j is (Han et al., 2012):

$$I_j = \sum_i w_{ij} O_i + \theta_j \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where,

w_{ij} is the weight of the connection from unit i in the previous layer to unit j.

O_i is the output of unit i, from the previous layer.

θ_j is the bias of the unit. The bias acts as a threshold in that it serves to vary the activity of the unit. This function is also referred to as a squashing function, because it maps a large input domain onto the smaller range of 0 to 1 (Han et al., 2012).

Given the net input I_j to unit j, then O_j , the output of unit j, is computed as:

$$O_j = \frac{1}{1 + e^{-I_j}} \quad \dots (5)$$

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

$$\mathrm{MAE} = \frac{1}{n}\sum_{i=1}^{n} |f_i - y_i| \quad \dots (6)$$

Where,
f_i = the predicted value.
y_i = the true value.

Mathematically, the mean squared error is represented thus (Mean Squared Error and Residual Sum of Squares, 2013):

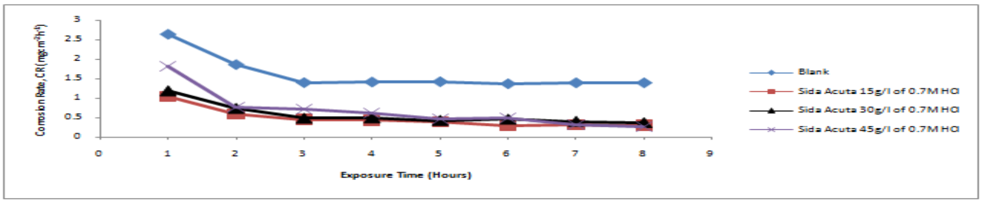
$$\mathrm{MSE} = \frac{1}{N}\sum (f_i - y_i)^2 \quad \dots (7)$$

Where,
$N = number\ of\ samples.$
$f_i = an\ estimator\ of\ parameter\ y_i.$
$y_i = true\ value.$

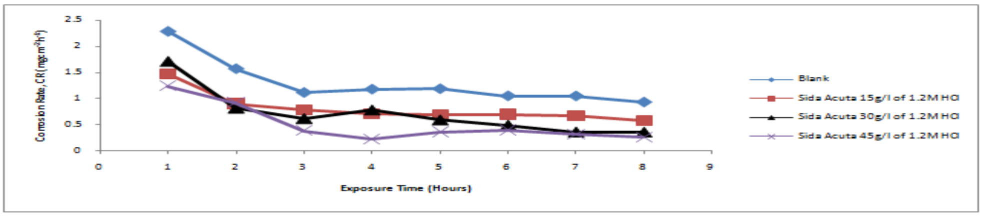
III. RESULTS

Table 1: Effect of addition of thoroughly pounded Sida Acuta's fresh leaves on the corrosion of mild steel coupons immersed in hydrochloric acid solution

Exposure Time (h)	0.7M HCl CR ($mgcm^{-2}h^{-1}$)	0.7M HCl I.E (%)	1.2M HCl CR ($mgcm^{-2}h^{-1}$)	1.2M HCl I.E (%)	2.2M HCl CR ($mgcm^{-2}h^{-1}$)	2.2M HCl I.E (%)
Addition of crushed leaves of Sida Acuta at 15g per litre of HCl						
1	1.0485	60.41	1.4638	35.96	4.1154	30.98
2	0.5925	68.22	0.9018	42.50	2.2973	35.69
3	0.4608	67.06	0.7803	29.76	1.5393	36.83
4	0.4378	69.03	0.7065	39.89	1.2082	36.58
5	0.4037	71.60	0.6901	41.70	0.9921	36.74
6	0.3006	78.03	0.6999	33.15	0.8766	34.88
7	0.3145	77.41	0.6647	36.37	0.7560	37.08
8	0.3129	77.54	0.5805	37.42	0.7435	35.85
Average	**0.4839**	**71.16**	**0.8110**	**37.09**	**1.5661**	**35.58**
Addition of crushed leaves of Sida Acuta at 30g per litre of HCl						
1	1.1792	55.48	1.7106	25.16	3.9847	33.17
2	0.7275	60.98	0.8103	48.33	2.0853	41.63
3	0.4724	66.23	0.6089	45.19	1.3205	45.81
4	0.4821	65.90	0.7740	34.14	1.0615	44.28
5	0.4200	70.43	0.5826	50.79	0.8051	48.66
6	0.4478	67.28	0.4811	54.05	0.6583	51.10
7	0.3946	71.66	0.3502	66.48	0.5145	57.18
8	0.3590	74.24	0.3471	62.58	0.4531	60.66
Average	**0.5603**	**66.53**	**0.7081**	**48.34**	**1.3604**	**47.81**
Addition of crushed leaves of Sida Acuta at 45g per litre of HCl						
1	1.8210	31.25	1.2359	45.93	4.0341	32.34
2	0.7667	58.88	0.9221	41.20	1.8544	48.09
3	0.7087	49.39	0.3892	64.97	1.3457	44.77
4	0.6190	56.21	0.2316	80.29	1.1726	38.45
5	0.4740	66.65	0.3694	68.80	0.9416	39.96
6	0.4903	64.17	0.4013	61.67	0.8694	35.42
7	0.3118	77.61	0.3170	69.66	0.5846	51.35
8	0.2672	80.82	0.2676	71.15	0.5290	54.08
Average	**0.6823**	**60.62**	**0.5168**	**62.96**	**1.4164**	**43.06**



(a)



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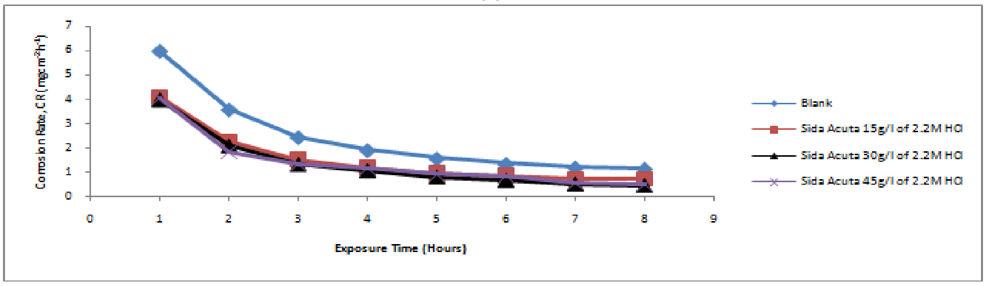
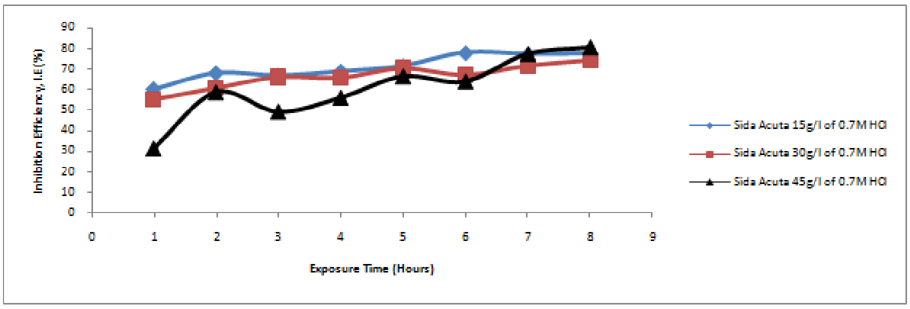


(c)

Figure 2: Effect of addition of thoroughly pounded fresh leaves of Sida Acuta on corrosion of mild steel coupons immersed at:
(a) 15g/l, 30g/l and 45g/l of 0.7M HCl
(b) 15g/l, 30g/l and 45g/l of 1.2M HCl
(c) 15g/l, 30g/l and 45g/l of 2.2M HCl



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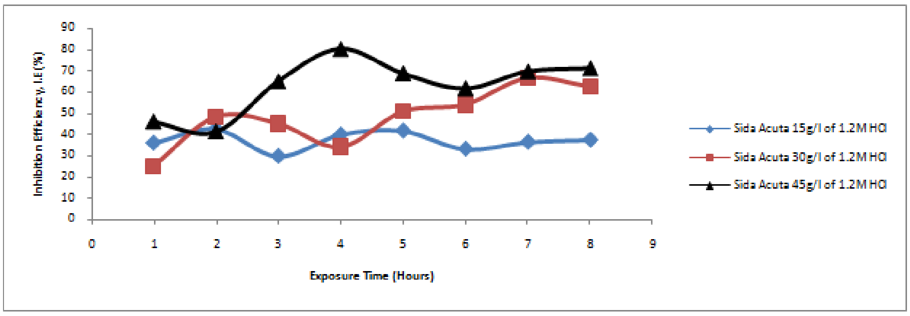

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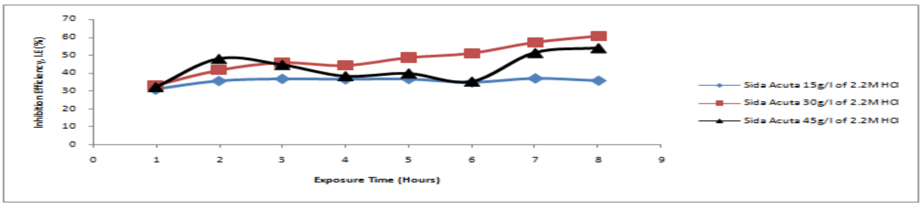


(c)

Figure 3: Sida Acuta's corrosion inhibition efficiency for mild steel coupons immersed at:
(a) 15g/l, 30g/l and 45g/l of 0.7M HCl
(b) 15g/l, 30g/l and 45g/l of 1.2M HCl
(c) 15g/l, 30g/l and 45g/l of 2.2M HCl

Table 2: Analysis for prediction of corrosion inhibition of mild steel by the crushed leaves of Sida Acuta in hydrochloric acid medium using multiple regression (MR)

	Model Coefficients			
	Constant	**Time (h)**	**Conc. of Acid (M)**	**Quantity of Crushed Leaves (g)**
HCl	1.721	-0.229	0.618	-0.019

Table 3: Analysis for prediction of corrosion inhibition of mild steel by the crushed leaves of Sida Acuta in hydrochloric acid medium using artificial neural network (ANN)

Independent variable importance for the addition of crushed fresh leaves of Sida Acuta in hydrochloric acid solution

	Importance	Normalized Importance
Time_of_Exposure	0.489	100.0%
Conc_of_HCl	0.250	51.2%
Quantity_of_Crushed_Leaves	0.262	53.5%

Parameter estimates for the addition of crushed fresh leaves of Sida Acuta in hydrochloric acid solution

Predictor		Predicted		
		Hidden Layer 1		Output Layer
		H(1:1)	H(1:2)	Exp_Corrosion_Rate
Input Layer	(Bias)	1.252	4.144	
	Time	-0.214	2.412	
	Conc_of_HCl	-0.156	-1.075	
	Quantity_of_Crushed_Leaves	2.012	-0.180	
Hidden Layer 1	(Bias)			3.313
	H(1:1)			-2.067
	H(1:2)			-4.518

Table 4: Error analysis for the prediction of corrosion inhibition of mild steel by thoroughly pounded leaves of Sida Acuta in hydrochloric acid solution 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	0.42538125	0.202978125
Mean Squared Error	0.378324713	0.078711839

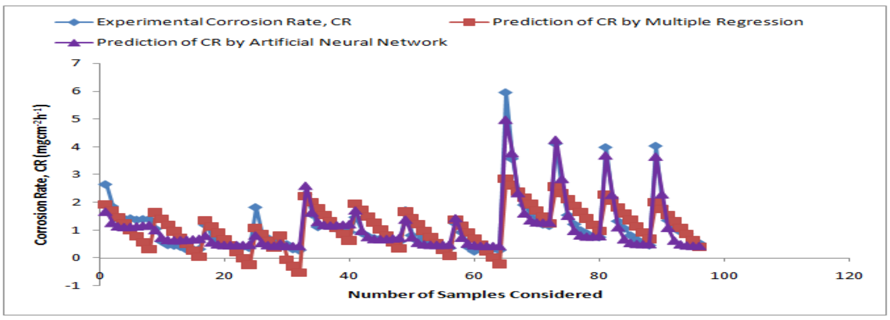


Figure 4: Comparison of error for the prediction of corrosion inhibition of mild steel by thoroughly crushed leaves of Sida Acuta in hydrochloric acid using multiple regression, MR and artificial neural network, ANN

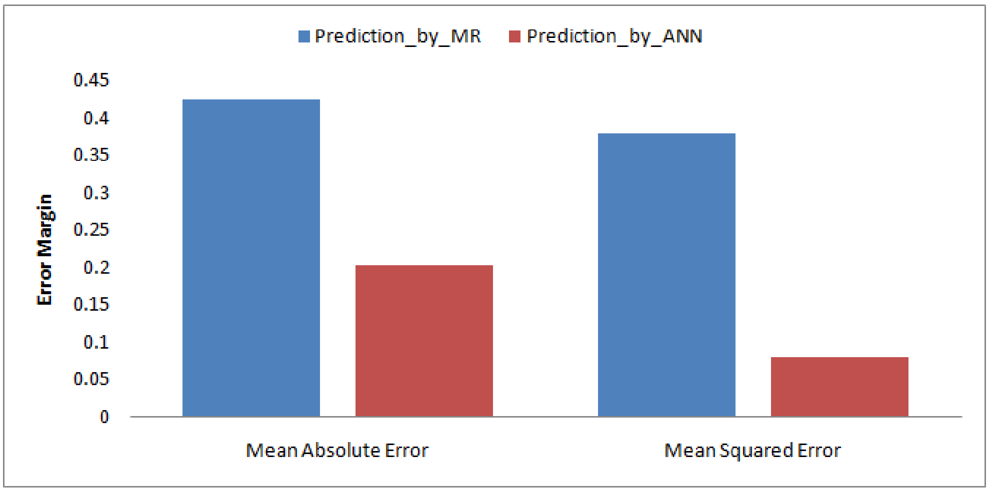


Figure 5: Error graph for the prediction of corrosion inhibition of mild steel in hydrochloric acid by thoroughly crushed leaves of Sida Acuta using multiple regression, MR and artificial neural network, ANN

Table 5: Effect of variation in temperature on the corrosion of mild steel coupons immersed in 0.7M HCl without and with 15g of thoroughly crushed Sida Acuta's fresh leaves

Temperature (K)	$CR_{SA\ addition}$ ($mgcm^{-2}h^{-1}$)	CR_{Blank} ($mgcm^{-2}h^{-1}$)	Log $CR_{SA\ addition}$	Log CR_{Blank}	1/T (K^{-1})
298	0.4839	1.6127	-0.3152	0.2076	0.003356
318	1.7391	5.4985	0.2403	0.7402	0.003145
338	2.6057	6.4186	0.4159	0.8074	0.002959
358	3.3718	7.0779	0.5279	0.8499	0.002793

$Slope_{Blank}$ = $-1092K^{-1}$
Activation Energy, Q = 20,908.68J

$Slope_{SA\ addition}$ = $-1467K^{-1}$
Activation Energy, Q = 28,088.86J

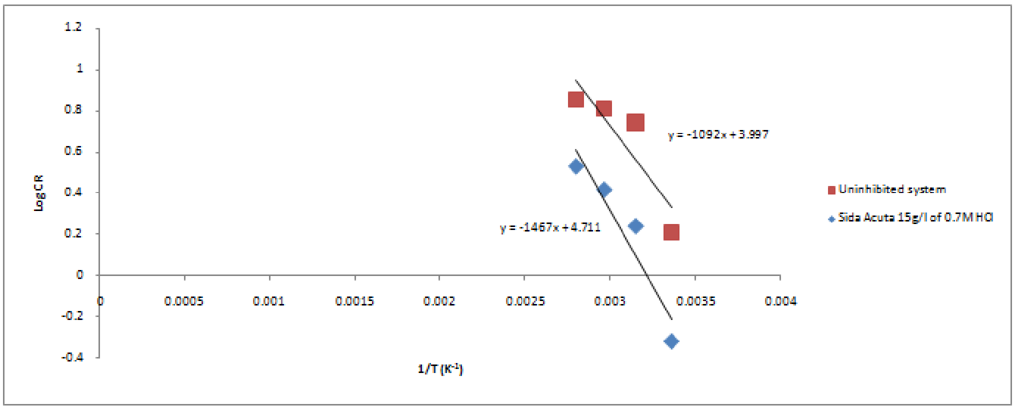


Figure 6: Arrhenius plot for the effect of variation in temperature on the corrosion of mild steel coupons immersed in 0.7M HCl without and with 15g of thoroughly crushed Sida Acuta's fresh leaves

Table 6: Calculated parameters of four adsorption isotherm models for adsorption of the thoroughly crushed fresh leaves of Sida Acuta onto the Surface of Mild Steel in Hydrochloric Acid medium.

Adsorption Isotherm							
Langmuir		**Freundlich**		**Temkin**		**El-Awady**	
Slope	**R^2**	**Slope**	**R^2**	**Slope**	**R^2**	**Slope**	**R^2**
1.771	0.996	-0.140	0.942	-0.092	0.952	-0.416	0.961
Parameters							
C (g)	**Log C**	**In C**	**□**	**C/□**	**Log □**	**1-□**	**Log (□/1-□)**
15	1.1761	2.7081	0.7116	21.0793	-0.1478	0.2884	0.3922
30	1.4771	3.4012	0.6653	45.0924	-0.1770	0.3347	0.2984
45	1.6532	3.8067	0.6062	74.2329	-0.2174	0.3938	0.1873

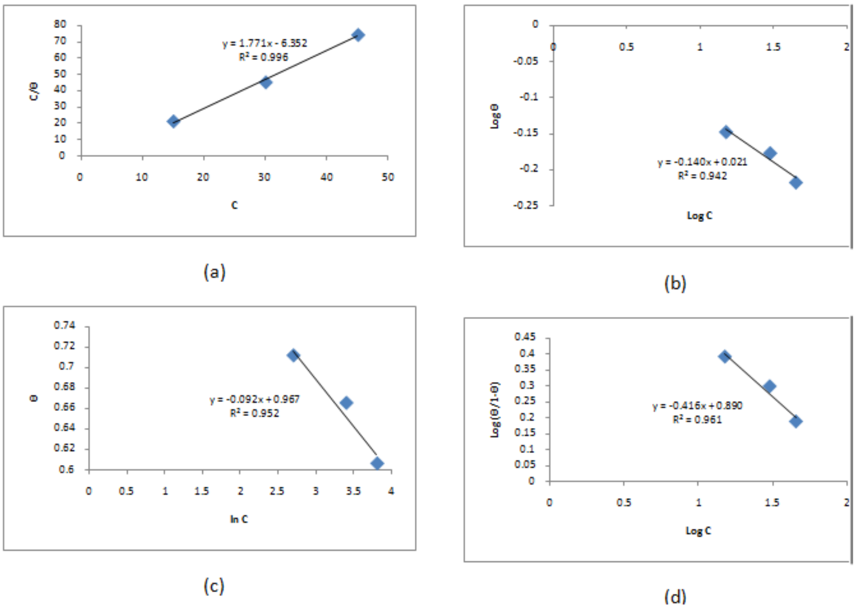


Figure 7: Adsorption isotherm models for adsorption of the thoroughly crushed fresh leaves of Sida Acuta on the mild steel surface in hydrochloric acid medium: (a) Langmuir Adsorption Isotherm; (b) Freundlich Adsorption Isotherm (c) Temkin Adsorption Isotherm (d) El-Awady Adsorption Isotherm

Table 7: Result of the phytochemical analysis conducted on Sida Acuta leaves

Plant Leaf		***Compounds***					
		Saponin (%)	*Tannin (%)*	*Flavonoid (%)*	*Alkanoid (%)*	*Phytate (%)*	*Phenol (ppm)*
Sida Acuta	*Dry*	1.73	1.522	2.50	4.00	0.717	22.19
	Fresh	0.98	0.657	2.00	3.10	0.597	20.55

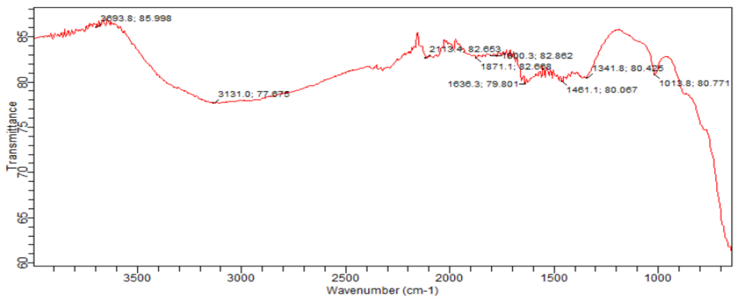
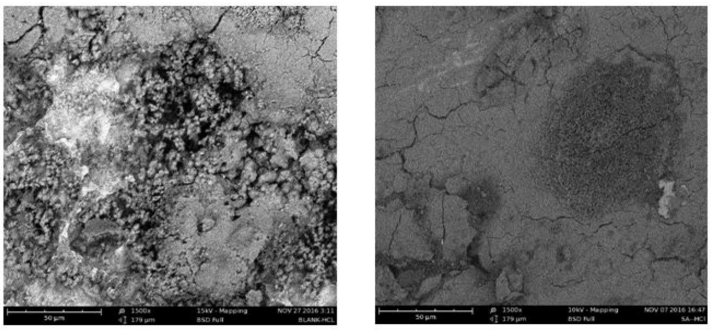


Figure 8: FTIR spectrum of film on mild steel surface after Immersion for eight hours in a medium containing the thoroughly crushed fresh leaves of Sida Acuta at 30g per litre of 0.7M HCl



(a) (b)

Figure 9: SEM characteristics of the corroded mild steel in; (a) the blank solution of 0.7M HCl (b) the presence of thoroughly pounded fresh leaves of Sida Acuta at 30g per litre of 0.7M HCl

IV. Discussion of Results

4.1 Effect of addition of thoroughly pounded fresh leaves of Sida Acuta on the corrosion of mild steel coupons immersed in hydrochloric acid solution

The addition of thoroughly pounded leaves of Sida Acuta was observed to reduce the corrosion of mild steel coupons immersed in hydrochloric acid medium. When the pounded leaves were added 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 were obtained in the order *CR (I.E)* as presented in Table 1: 0.4839mgcm^{-2}h^{-1} (71.16%) in 0.7M HCl; 0.8110mgcm^{-2}h^{-1} (37.09%) in 1.2M HCl and 1.5661 mgcm^{-2}h^{-1} (35.58%) in 2.2M HCl. When the addition of the crushed fresh leaves of sida Acuta was increased to 30g per litre of various acid concentrations, the corresponding average corrosion rate and inhibition efficiency were: 0.5603mgcm^{-2}h^{-1} (66.53%) in 0.7M HCl; 0.7081mgcm^{-2}h^{-1} (48.34%) in 1.2M HCl and 1.3604mgcm^{-2}h^{-1} (47.81%) in 2.2M HCl. Further addition of the pounded fresh leaves of Sida Acuta at 45g per litre of 0.7M, 1.2M and 2.2M HCl gave the following average corrosion rate and inhibition efficiency: 0.6823mgcm^{-2}h^{-1} (60.62%) in 0.7M HCl; 0.5168mgcm^{-2}h^{-1} (62.96%) in 1.2M HCl and 1.4164mgcm^{-2}h^{-1} (43.06%) in 2.2M HCl. The corrosion rate was observed to increase with increase in acid concentration. This development reveals that the corrosive environment becomes more aggressive as the concentration of acid is increased.

The corrosion rate–time curves for the mild steel coupons immersed in *0.7M, 1.2M* and *2.2M* HCl with and without the addition of thoroughly crushed Sida Acuta's fresh leaves are shown in Figure 2. Generally, the corrosion rate curves were observed to progressively decrease with increase in time. Figure 3 shows the inhibition efficiency for the corrosion of mild steel coupons immersed in 0.7M, 1.2M and 2.2M HCl as a result of the addition of crushed leaves of Sida Acuta at 15g per litre, 30g per litre and 45g per litre of the acid concentration. The inhibition efficiency–time curve was observed to increase as the experimentation progressed. For the entire examined environment, the maximum inhibition efficiency of 71.16% was attained when the thoroughly pounded leaves of Sida Acuta were added at 15g per litre of 0.7M HCl whilst the corrosion rate reduced from 1.0485 to 0.3006mgcm^{-2}h^{-1}.

4.2 Prediction of corrosion inhibition of mild steel in hydrochloric acid medium by the thoroughly crushed leaves of Sida Acuta

Multiple regression and artificial neural network were used to predict the corrosion rates of mild steel coupons in the presence and absence of thoroughly squeezed leaves of Sida Acuta in hydrochloric acid medium with the aid of the SPSS software. The predicted values are shown in Appendix 1.

Using multiple regression as illustrated in Table 2, the predictive equation for the addition of the crushed fresh leaves of Sida Acuta to the hydrochloric acid medium is stated thus:

$$CR_{SA\ in\ HCl\ by\ MR} = 1.721 - 0.229(\text{time}) + 0.618(\text{conc. of acid}) - 0.019(\text{quantity of crushed leaves}) \quad \ldots\ldots\ (8)$$

The prediction of the experimental corrosion rate by the artificial neural network reveals the importance of independent variables (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}) for the addition of crushed leaves of Sida Acuta to the hydrochloric acid induced corrosion of mild steel as presented in Table 3. The time of exposure immensely contributed to the prediction of the corrosion rate by 48.9%, followed by the quantity of crushed leaves, 26.2% and finally the concentration of acid, 25.0%.

The comparison of error results for the prediction of corrosion inhibition of mild steel by the crushed leaves of Sida Acuta in hydrochloric acid medium using multiple regression and artificial neural network are presented in Table 4 and displayed in Figures 4 and 5. The results show that the predictions by the artificial neural network did not only give minimal errors but were closer to the experimental corrosion rate values in comparison with the predictions by multiple regression.

4.3 Temperature dependence

The result of the variation in temperature between 298K and 358K on the corrosion of mild steel without and with the addition of the crushed leaves of Sida Acuta at 15g per litre of 0.7M HCl agrees with the Arrhenius relationship and is presented in Table 5 and displayed in Figure 6. The activation energy for the corrosion of mild steel in the blank solution of 0.7M HCl was 20,908.68J whilst the addition of Sida Acuta's pounded leaves increased the activation energy to 28,088.86J. This higher value of activation energy obtained by the introduction of the crushed plant leaves to the corrodent reveals that higher energy needs to be attained before further corrosion can take place.

4.4 Adsorption isotherm consideration

Langmuir, Freundlich, Temkin and El-Awady adsorption isotherm models were tested and presented in Table 6 and Figure 7. The results show that the corrosion inhibition of mild steel in hydrochloric acid by the crushed leaves of Sida Acuta obeys all the aforementioned isotherm models with the Langmuir isotherm maintaining the best fit of $R^2 = 0.996$; El-Awady, $R^2 = 0.961$; Temkin, $R^2 = 0.952$ and Freundlich, $R^2 = 0.942$. Equations (9), (10), (11) and (12) illustrate these adsorption isotherm models (Adejo et al., 2013; Fadare et al., 2016).

Langmuir: $$\frac{C}{\theta} = C + \frac{1}{K} \quad (9)$$

Freundlich: $$\text{Log}\Theta = \text{Log}K + n\text{Log}C \quad (10)$$

El-Awady: $$Log\left(\frac{\theta}{1-\theta}\right) = LogK + yLogC \quad (11)$$

Temkin: $$\Theta = bInA + bInC \quad (12)$$

Where,
θ is the fraction of surface coverage,
C is the inhibitor concentration,
K is the equilibrium constant for the adsorption/desorption process, and
b = Constant related to heat of sorption (J/mol).

4.5 Phytochemical analysis of the leaves of Sida Acuta

The phytochemical analysis of Sida Acuta's leaves as illustrated in Table 7 indicates the presence of alkanoid (4.0%), tannin (1.522%), saponin (1.73%), phytate (0.717%), flavonoid (2.50%) 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

Figure 8 shows the FTIR spectrum of the protective film that adhered on the surface of mild steel coupon owing to the addition of the crushed leaves of Sida Acuta at 30g per litre of 0.7M HCl for eight hours. The strong band at $3693.8cm^{-1}$ reveals the functional group of hydrogen atom bonded to oxygen atom (O–H stretching vibration). The strong bands at frequencies $2113.4cm^{-1}$, $1871.1cm^{-1}$ and $1636.3cm^{-1}$ indicate the presence of C≡C, C=O and C=C stretching vibrations of alkynes, acid anhydride and alkene respectively. CH_2 bending is also spotted around $1461.1cm^{-1}$.

4.7 SEM micrograph for the corrosion inhibition of mild steel in HCl solution by the crushed leaves of Sida Acuta

Figure 9(a) shows the SEM image of the corrosion of mild steel in an uninhibited solution of 0.7M HCl. Corrosion was observed not to take place identically over the surface of the steel. However, the addition of the crushed fresh leaves of Sida Acuta at 30g per litre of 0.7M HCl clearly protected the surface of the steel from corrosion as shown in Figure 9(b) in comparison with the inhibitor-free solution.

V. CONCLUSION

1. The corrosion rate was observed to increase with increase in acid concentration.
2. The maximum inhibition efficiency of 71.16% was attained when the thoroughly pounded leaves of Sida Acuta were added at 15g per litre of 0.7M HCl whilst the corrosion rate reduced from 1.0485 to $0.3006mgcm^{-2}h^{-1}$.
3. Predictions by the artificial neural network gave minimal errors and were closer to the experimental corrosion rate values in comparison with the predictions by multiple regression.
4. The corrosion inhibition of mild steel in hydrochloric acid by the crushed leaves of Sida Acuta obeys all the four tested adsorption isotherm models with the Langmuir isotherm maintaining the best fit of $R^2 = 0.996$; El-Awady, $R^2 = 0.961$; Temkin, $R^2 = 0.952$ and Freundlich, $R^2 = 0.942$.
5. The FTIR analysis revealed that the adsorbed constituents of the crushed leaves of Sida Acuta on the surface of mild steel are associated with the stretching vibrations of C≡C, C=C, C=O and O–H bonds.
6. The SEM image shows that the degradation of the surface of mild steel in an uninhibited 0.7M HCl solution is localized. However, the addition of Sida Acuta's crushed leaves remarkably prevented the surface of the steel from corrosion.

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Appendix 1: Prediction of corrosion inhibition of mild steel in hydrochloric acid medium by thoroughly crushed leaves of Sida Acuta

Case	Time (h)	Conc_of HCl (M)	Quantity_of_SA_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	2.6487	1.9249	0.7238	1.6707	0.978
2	2	0.7	0	1.8646	1.6961	0.1685	1.2657	0.5989
3	3	0.7	0	1.3989	1.4673	-0.0684	1.143	0.2559
4	4	0.7	0	1.4137	1.2386	0.1751	1.1171	0.2966
5	5	0.7	0	1.4214	1.0098	0.4116	1.1245	0.2969
6	6	0.7	0	1.3684	0.7810	0.5874	1.1433	0.2251
7	7	0.7	0	1.3924	0.5522	0.8402	1.1657	0.2267
8	8	0.7	0	1.3934	0.3235	1.0699	1.1888	0.2046
9	1	0.7	15	1.0485	1.6408	-0.5923	1.0049	0.0436
10	2	0.7	15	0.5925	1.4120	-0.8195	0.7331	-0.1406
11	3	0.7	15	0.4608	1.1833	-0.7225	0.6556	-0.1948
12	4	0.7	15	0.4378	0.9545	-0.5167	0.6397	-0.2019
13	5	0.7	15	0.4037	0.7257	-0.3220	0.6452	-0.2415
14	6	0.7	15	0.3006	0.4970	-0.1964	0.6591	-0.3585
15	7	0.7	15	0.3145	0.2682	0.0463	0.6767	-0.3622
16	8	0.7	15	0.3129	0.0394	0.2735	0.6963	-0.3834
17	1	0.7	30	1.1792	1.3567	-0.1775	0.8017	0.3775
18	2	0.7	30	0.7275	1.1280	-0.4005	0.5636	0.1639
19	3	0.7	30	0.4724	0.8992	-0.4268	0.4932	-0.0208
20	4	0.7	30	0.4821	0.6704	-0.1883	0.4722	0.0099
21	5	0.7	30	0.4200	0.4417	-0.0217	0.4673	-0.0473
22	6	0.7	30	0.4478	0.2129	0.2349	0.4682	-0.0204
23	7	0.7	30	0.3946	-0.0159	0.4105	0.4714	-0.0768
24	8	0.7	30	0.3590	-0.2447	0.6037	0.4756	-0.1166
25	1	0.7	45	1.8210	1.0727	0.7483	0.8123	1.0087

26	2	0.7	45	0.7667	0.8439	-0.0772	0.5461	0.2206
27	3	0.7	45	0.7087	0.6151	0.0936	0.4673	0.2414
28	4	0.7	45	0.6190	0.3864	0.2326	0.4423	0.1767
29	2	0.7	45	0.4740	0.7982	-0.3242	0.5222	-0.0482
30	6	0.7	45	0.4903	-0.0712	0.5615	0.4318	0.0585
31	7	0.7	45	0.3118	-0.2999	0.6117	0.4314	-0.1196
32	8	0.7	45	0.2672	-0.5287	0.7959	0.4318	-0.1646
33	1	1.2	0	2.2857	2.2341	0.0516	2.6014	-0.3157
34	2	1.2	0	1.5683	2.0053	-0.4370	1.6442	-0.0759
35	3	1.2	0	1.1109	1.7765	-0.6656	1.2976	-0.1867
36	4	1.2	0	1.1753	1.5477	-0.3724	1.1938	-0.0185
37	5	1.2	0	1.1838	1.3190	-0.1352	1.1733	0.0105
38	6	1.2	0	1.0470	1.0902	-0.0432	1.1815	-0.1345
39	7	1.2	0	1.0447	0.8614	0.1833	1.1993	-0.1546
40	8	1.2	0	0.9276	0.6327	0.2949	1.2200	-0.2924
41	1	1.2	15	1.4638	1.9500	-0.4862	1.7128	-0.2490
42	2	1.2	15	0.9018	1.7212	-0.8194	0.9822	-0.0804
43	3	1.2	15	0.7803	1.4924	-0.7121	0.7524	0.0279
44	4	1.2	15	0.7065	1.2637	-0.5572	0.6887	0.0178
45	5	1.2	15	0.6901	1.0349	-0.3448	0.6788	0.0113
46	6	1.2	15	0.6999	0.8061	-0.1062	0.6881	0.0118
47	7	1.2	15	0.6647	0.5774	0.0873	0.7050	-0.0403
48	8	1.2	15	0.5805	0.3486	0.2319	0.7253	-0.1448
49	1	1.2	30	1.7106	1.6659	0.0447	1.3842	0.3264
50	2	1.2	30	0.8103	1.4372	-0.6269	0.745	0.0653
51	3	1.2	30	0.6089	1.2084	-0.5995	0.5524	0.0565
52	4	1.2	30	0.7740	0.9796	-0.2056	0.4953	0.2787
53	5	1.2	30	0.5826	0.7508	-0.1682	0.4789	0.1037
54	6	1.2	30	0.4811	0.5221	-0.0410	0.4762	0.0049
55	7	1.2	30	0.3502	0.2933	0.0569	0.4784	-0.1282
56	8	1.2	30	0.3471	0.0645	0.2826	0.4827	-0.1356
57	1	1.2	45	1.2359	1.3819	-0.1460	1.4350	-0.1991
58	2	1.2	45	0.9221	1.1531	-0.2310	0.7369	0.1852
59	3	1.2	45	0.3892	0.9243	-0.5351	0.5252	-0.1360
60	4	1.2	45	0.2316	0.6956	-0.4640	0.4617	-0.2301
61	5	1.2	45	0.3694	0.4668	-0.0974	0.4414	-0.0720
62	6	1.2	45	0.4013	0.2380	0.1633	0.4350	-0.0337
63	7	1.2	45	0.317	0.0092	0.3078	0.4333	-0.1163
64	8	1.2	45	0.2676	-0.2195	0.4871	0.4333	-0.1657
65	1	2.2	0	5.9626	2.8524	3.1102	4.9762	0.9864
66	2	2.2	0	3.5723	2.6236	0.9487	3.7766	-0.2043
67	3	2.2	0	2.4367	2.3949	0.0418	2.3381	0.0986
68	4	2.2	0	1.9052	2.1661	-0.2609	1.6102	0.2950
69	5	2.2	0	1.5683	1.9373	-0.3690	1.3596	0.2087
70	6	2.2	0	1.3462	1.7086	-0.3624	1.2859	0.0603
71	7	2.2	0	1.2016	1.4798	-0.2782	1.2732	-0.0716
72	8	2.2	0	1.1519	1.2510	-0.0991	1.2812	-0.1293
73	1	2.2	15	4.1154	2.5684	1.5470	4.2585	-0.1431
74	2	2.2	15	2.2973	2.3396	-0.0423	2.8500	-0.5527
75	3	2.2	15	1.5393	2.1108	-0.5715	1.5276	0.0117
76	4	2.2	15	1.2082	1.882	-0.6738	0.9817	0.2265
77	5	2.2	15	0.9921	1.6533	-0.6612	0.8160	0.1761
78	6	2.2	15	0.8766	1.4245	-0.5479	0.7747	0.1019
79	7	2.2	15	0.756	1.1957	-0.4397	0.7754	-0.0194
80	8	2.2	15	0.7435	0.9670	-0.2235	0.7915	-0.0480
81	1	2.2	30	3.9847	2.2843	1.7004	3.6928	0.2919
82	2	2.2	30	2.0853	2.0555	0.0298	2.2747	-0.1894
83	3	2.2	30	1.3205	1.8268	-0.5063	1.1072	0.2133
84	4	2.2	30	1.0615	1.5980	-0.5365	0.6734	0.3881
85	5	2.2	30	0.8051	1.3692	-0.5641	0.5458	0.2593
86	6	2.2	30	0.6583	1.1404	-0.4821	0.5086	0.1497
87	7	2.2	30	0.5145	0.9117	-0.3972	0.4999	0.0146
88	8	2.2	30	0.4531	0.6829	-0.2298	0.5013	-0.0482
89	1	2.2	45	4.0341	2.0002	2.0339	3.6514	0.3827
90	2	2.2	45	1.8544	1.7715	0.0829	2.2930	-0.4386
91	3	2.2	45	1.3457	1.5427	-0.1970	1.0923	0.2534
92	4	2.2	45	1.1726	1.3139	-0.1413	0.6317	0.5409
93	5	2.2	45	0.9416	1.0851	-0.1435	0.4968	0.4448
94	6	2.2	45	0.8694	0.8564	0.0130	0.4553	0.4141
95	7	2.2	45	0.5846	0.6276	-0.0430	0.4421	0.1425
96	8	2.2	45	0.5290	0.3988	0.1302	0.4384	0.0906