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Development of Predictive Mathematical Model using Scent Leaf, Cassava Leaf and Neem Leaf Extracts as Corrosion Inhibitors on Mild Steel in Seawater and Sodium Chloride Environments

Nairobi Cletus Madawa [1,*], Emomotimi Amula [1] and Promise Mebine [2]

[1] *Department of Mechanical Engineering, Niger Delta University, Wilberforce Island, Amassoma, Bayelsa State, Nigeria.*
[2] *Director/Chief Executive, National Mathematical Center, Abuja, Nigeria.*

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Abstract

Mathematical Model is a statistical tool used to evaluate the rate of corrosion on oil and gas pipeline and proffer corrosion inhibitor to mitigate corrosion on the material. Experimental values were utilized to achieve predictive values. The tool enables us to deduce values on the pipeline where experimental values are not available. Maple Software was the basic tool used to perform the analysis. Weight loss method was utilized to obtain the experimental values which were further applied to determine the predictive values by using Mean Square Error (MSE), Evaluation of Accuracy on Prediction, Multiple Absolute Errors (MAE), Multiple Regression Analysis (MRA) and Polynomial Equation. Green plant extracts like Scent Leaf (SL), Cassava Leaf (CL) and Neem Leaf (NL) extracts were served as corrosion inhibitors which were added to these corrosive environments, Seawater, SW and Sodium Chloride, NaCl. The Mild Steel C-1026 coupons were immersed in the various solutions for 100 days. The results obtained from the study on weight loss of Seawater and Sodium Chloride was 0.271 and 0.193. Then the Weight loss on MSE analysis show that Seawater had both experimental and predictive values as 0.48 and 0.048008474 with an error of 0.0008474, while Sodium Chloride had 0.32 and 0.32007343 with error of 0.0007343 respectively. The evaluation of accuracy on prediction, EAP of weight loss in Seawater had 0.48 and 0.48008474 with error of 0.0008474, and Sodium Chloride has 0.32 and 0.32007343 with error of 0.00007343. Deducing from the analysis, the errors obtained from the MSE and EAP were very minimal. Therefore, Mathematical model is ideal for the prediction of pipeline corrosion and maintenance.

Keywords: Mathematical Model; Maple Software; Experimental Value; Predictive Value; Corrosion Inhibitor

1. Introduction

In the construction of crude oil pipeline, Mild Steel is frequently used for its fabrication. This material is very much exposed to various types of corrosive media. The material is often laid underground whereby the nature of soil is identified as a major cause of corrosion on it (Uko et al, 2014; Uhlig. 1973; Ekot. 2012; Madawa et al, 2021). Corrosion is classified as a gradual depreciation of metal by diverse electrochemical reaction between the metal and its environment (Tuaweri et al, 2015; Madawa and Amula, 2024; Ambrish et al, 2012). When corrosion takes place on the crude oil pipeline in the underground, there is complexity in detecting the rate of corrosion at regular interval. In order to alleviate this intricacy, predictive mathematical model has been developed. It is designed to determine the weight loss or corrosion rate of the metal using experimental values. Also, the model is used to enable visualization (i.e., for interpolation and extrapolation) and to infer values where experimental values are not available. Furthermore, the model summarizes the relationship among the values of the experiment.

*Corresponding author: Nairobi Cletus Madawa

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As a matter of fact, corrosion poses a great threat to the oil and gas industry all over the world because of the enormous losses of the natural resources and finance associated with corrosion, and as such, protection against these menaces is increasing geometrically (Madawa and Amula, 2024; Oguzie. 2008). Consequently, inhibitors are applied in the process to mitigate corrosion. Inhibitor is said to be a substance when added to a system in small concentration reduces the corrosion rate of the metal (Tuaweri et al, 2015; Madawa and Amula, 2024; Ambrish et al, 2012). Initially, inorganic compounds were intensively utilized as corrosion inhibitors, such as chromate, arsenate, etc. These compounds have some adverse effects on human being and the environment most especially the toxicity and high cost (Madawa et al, 2021; Madawa and Amula, 2024; Ameena, 2015). Therefore, researchers have sought for alternative to mitigate corrosion by using green plants. Vast numbers of green plants have been studied by different researchers that proved to be very efficient. According to Madawa *et al*, and Oguzie (Madawa et al, 2021; Madawa and Amula, 2024, and Oguzie. 2008), researchers unanimously consented that most green plant extracts are green corrosion inhibitors because they are biodegradable, less toxic and do not contain heavy metals. Literature on corrosion and corrosion inhibitors using green plant extracts are accessible to Sanjay, *et al*., (Sanjay et al, 2015); Khadom *et al*, (2015); Hassan *et al*, (2020); Felintola *et al*, (2019); Tuaweri and Ogbonnaya, (2017); Tuaweri *et al*, (2015); Ndukwe. (2017); Suleiman *et al*, (2017); Anyanwu *et al*, (2014); Okafor *et al*, (2010); Thangavelu *et al*, (2011); Ejieh and Ejimofor (2012); Umoren and Udoh. (2011); Anyakwo (2007), etc.

In this study, green plant extracts such as Scent Leaf (SL), Cassava Leaf (CL) and Neem Leaf (NL) extracts were investigated to alleviate corrosion on Mild Steel C-1026 oil and gas pipeline in Seawater (SW) and Sodium Chloride (NaCl). These corrosive media are used because they are predominately found in the soil where oil and gas pipelines are laid continuously.

However, the monitoring, maintaining and determining corrosion rate of the pipeline in the ground at regular interval poses great intricacy. Technology has advanced a means of monitoring the corrosion rate on oil and gas pipeline with the application of predictive Mathematical Model. This approach enables the operators of the facilities to determine corrosion rate and predetermine the interval for maintenance to be carried out from the data obtained on areas where data were acquired and not acquired. The experimental data is the prime factor in predictive mathematical modeling. There are various approaches to the achievement of Mathematical Model, thus; Polynomial Equation, Multiple Regression Analysis (MRA), Mean Square Error (MSE) and Evaluation of Accuracy on Prediction of Corrosive media.

2. Materials and methods

2.1. Preparation of Mild Steel C-1026 Specimen

The chemical composition of Mild Steel, MS C-1026 specimen of 1cm oil and gas pipeline comprises: 0.08% Mn, 0.17% Ti, 0.07% As, 0.07% Cu, and 98.88% Fe (Madawa et al, 2021, Madawa and Amula, 2024). This MS was cut with cutting machine into 2cm × 4cm sizes. The coupons were abraded with Carborandium paper to mirror finish and degreased with acetone to reduce the necessary impurities to the lowest level, and then utilized for the weight loss analysis and examination of the surfaces (Madawa et al, 2021; Madawa and Amula, 2024).

2.2. Preparation of Leaf Paste

The green plants, Scent leaf, Cassava Leaf and Neem Leaf extracts weighing 31g were pound with mortar and pestle. 150ml of the plant extract solution was filtered and mixed with 250ml of Seawater and 3.5wt% of NaCl (Madawa et al, 2021; Madawa and Amula, 2024).

2.3. Weight Loss Method

The Mild Steel C-1026 specimens were immersed in 400ml of the various plant extracts and corrosive media solutions for 100 days (2400 hours). However, the Corrosion Rate, CR and Inhibition Efficiency, (IE %) were calculated with the following formulae:

$$Corrosion\ Rate, CR = \frac{K \times Loss\ in\ weight\ (g)}{Surface\ Area\ (A) \times Period\ of\ immersion\ (Hr)\ of\ specimen \times Density\ (\rho)\ of\ Mild\ Steel}$$

$$CR = \frac{K(Wlos)}{AT\rho}$$

$$= \frac{K(W2-W1)}{AT\rho} \quad (1)$$

Where,

W_1 - W_2 = Weight loss in g, D (ρ) = Density of Mild Steel (7.86g/cm^3 for Mild Steel), A = Area in cm^2, T = Exposure Time in hours (Madawa et al, 2021; Tuaweri et al, 2015; Madawa and Amula, 2024; Anyanwu et al, 2014).

$$Corrosion\ Inhibition\ Efficiency, IE(\%) = 100\left[\frac{1-W2}{W1}\right]\% \quad (2)$$

Where, W_1 and W_2 are weight loss in Mild Steel in the absence and presence of inhibitors (Madawa et al, 2021; Tuaweri et al, 2015; Madawa and Amula, 2024; Thangavelu et al, 2011).

2.4. Polynomial Equation

This is an equation with multiple terms made of numbers and variables. It has root which values are x and y, where y = 0 (HSCALPE). Moreover, it is formed with variables, exponents and coefficients. Polynomial equation consist number of exponents, where the higher one is classified as the degree of the equation (BCMPE).

$$ax^6 + bx^5 + cx^4 + dx^3 + ex^2 + fx + g = 0 \quad (3)$$

In this investigation, equation (4) was applied instead of the general equation (Ekot. 2012). The application of equation (Madawa et al, 2021) is because it contained 10 numbers. The variables, time and weight loss were derived from the exponents. Thus:

$$at^9 + bt^8 + ct^7 + dt^6 + et^5 + ft^4 + gt^3 + ht^2 + it + j = 0 \quad (4)$$

2.5. Multiple Regression Analysis (MRA)

Regression analysis is a statistical tool for investigation between variables (Sykes. 1992). Laerd Statistics, (2013), stated that regression is an extension of simple linear regression. MRA is applied whenever there is an intention to predict variables of two or more values.

2.6. Mean Squared Error (MSE)

MSE is the procedure to estimate an unobserved quantity which measures the average squares of the error. More precisely, it is the average squared difference between the estimated values and actual values. Furthermore, MSE tells us the closeness of a regression (fitted) line to the set (data) points (Ndukwe. 2017). The formula for Mean Square Error is shown as:

$$MSE = \frac{1}{n}\sum_{i=1}^{n}(\gamma - \gamma^1)2 \quad (5)$$

Where, n is time, y is experimental value, y^1 is predicted value.

2.7. Mean Absolute Error (MAE)

This analysis process tells the extent of variation between the predicted values and experimental values. That is, the difference between the forecast and observed values (Ndukwe. 2017).

2.8. Evaluation of Accuracy on Prediction of Corrosive Media

Evaluation of Accuracy on Prediction is a statistics tool that states the ratio of error of the absolute value to the actual experimental value.

3. Results

3.1. Corrosive Media - Weight Loss Analysis

Table 1 Weight Loss of Mild Steel C-1026 in different Corrosive Media without corrosion inhibitor

Weight loss/Medium		
Exposure Time	SW	NaCl
240	0.05	0.05
480	0.09	0.08
720	0.16	0.12
960	0.19	0.16
1200	0.29	0.12
1440	0.31	0.22
1680	0.34	0.26
1920	0.36	0.28
2160	0.44	0.32
2400	0.48	0.32
Average	0.271	0.193

Table 2 Weight Loss of Mild Steel C-1026 in SW and 3.5wt% of Baths with Scent Leaf, Cassava Leaf and Neem Leaf extracts

Exposure Time	**SW**	**NaCl**
Average	0.271	0.193
Addition of Leaf-paste of Scent Leaf		
240	0.03	0.04
480	0.02	0.06
720	0.01	0.09
960	0.03	0.09
1200	0.05	0.12
1440	0.11	0.15
1680	0.06	0.17
1920	0.21	0.23
2160	0.19	0.25
2400	0.22	0.28
Average	0.093	0.148
Addition of Leaf-paste of Cassava Leaf		
240	0.04	0.03
480	0.06	0.06

720	0.04	0.08
960	0.02	0.08
1200	0.01	0.08
1440	0.03	0.09
1680	0.06	0.10
1920	0.09	0.09
2160	0.12	0.1
2400	0.17	0.12
Average	0.064	0.083
Addition of Leaf-paste of Neem Leaf		
240	0.02	0.02
480	0.03	0.06
720	0.01	0.06
960	0.01	0.09
1200	0.01	0.08
1440	0.01	0.09
1680	0	0.1
1920	0	0.11
2160	0.05	0.11
2400	0.08	0.14
Average	0.022	0.086

Table 3 Inhibition Efficiency of Corrosion Inhibitors on Mild Steel C-1026 in different Corrosive Media

S/No	**Media**	**Average Inhibition Efficiency, IE (%)**
1	SW + SL	96.54
2	SW + CL	96.51
3	SW + NL	96.82
4	NaCl + SL	97.29
5	NaCl + CL	97.58
6	NaCl + NL	97.42

3.2. Mean Square Error (MSE)

Table 4 Mean Square Error (MSE) of Seawater

Time (χ)	Weight Loss (□)	Predicted Value (□/)	Error (□ − □/)	Error Squared
1	0.05	0.05000000	0	0
2	0.09	0.09000000	0	0
3	0.16	0.16000007	0.00000007	$7e^{-08}$
4	0.19	0.19000014	0.00000014	$1.4e^{-07}$
5	0.29	0.29000264	0.00000264	$2.64e^{-06}$
6	0.31	0.31000224	0.00000224	$2.24e^{-06}$
7	0.34	0.34001654	0.00001654	$1.654e^{-05}$
8	0.36	0.36002894	0.00002894	$2.894e^{-05}$
9	0.44	0.44004434	0.00004434	$4.434e^{-05}$
10	0.48	0.48008474	0.00008474	$8.474e^{-05}$

3.3. Mean Square Error (MSE)

Table 5 Mean Square Error (MSE) of Sodium Chloride

Time (χ)	Weight Loss (□)	Predicted Value (□/)	Error (□ − □/)	Error Squared
1	0.05	0.05000000	0	0
2	0.08	0.08000001	0.00000001	1^{-15}
3	0.12	0.11999983	0.00000017	2.89^{-13}
4	0.16	0.15999893	0.00000107	1.1449^{-11}
5	0.12	0.11999923	0.00000077	5.929^{-12}
6	0.22	0.22000583	0.00000583	3.39889^{-10}
7	0.26	0.26001153	0.00001153	1.329409^{-9}
8	0.28	0.27998613	0.00001387	1.923769^{-9}
9	0.32	0.31994383	0.00005617	3.1550689^{-8}
10	0.32	0.32007343	0.00007343	5.3919649^{-8}

3.4. Evaluation of Accuracy on Prediction of Corrosive Media Corrosive Media and Corrosion Inhibitors Analysis

Table 6 Evaluation of Accuracy on Prediction of weight loss on Mild Steel C-1026 in Corrosive Media

Time	Experimental Value	Predicted Value	Error
SW			
1	0.05	0.05000000	0
2	0.09	0.09000001	$1e^{-08}$
3	0.16	0.16000007	$7e^{-08}$

4	0.19	0.19000014	$1.4e^{-07}$
5	0.29	0.29000264	$2.64e^{-06}$
6	0.31	0.31000224	$2.24e^{-06}$
7	0.34	0.34001654	$1.654e^{-05}$
8	0.36	0.36002894	$2.894e^{-05}$
9	0.44	0.44004434	$4.434e^{-05}$
10	0.48	0.48008474	$8.474e^{-04}$
NaCl			
1	0.05	0.05000000	0
2	0.08	0.08000001	$1e^{-08}$
3	0.12	0.11999983	$1.7e^{-07}$
4	0.16	0.15999893	$1.07e^{-06}$
5	0.12	0.11999923	$7.7e^{-07}$
6	0.22	0.22000583	$5.83e^{-06}$
7	0.26	0.26001153	$1.15e^{-05}$
8	0.28	0.27998613	$1.387e^{-05}$
9	0.32	0.31994383	$5.617e^{-05}$
10	0.32	0.32007343	$7.343e^{-05}$

3.5. Corrosion Inhibition Analysis

Table 7 Evaluation of Accuracy on Prediction of weight loss on Mild Steel C-1026 in Corrosive Media with Corrosion Inhibition

Time	Experimental Value	Predicted Value	Error
SW + SL			
1	0.03	0.03	0
2	0.02	0.02	$1e^{-8}$
3	0.01	0.0099998	$1.7e^{-7}$
4	0.03	0.0299994	$5.7e^{-7}$
5	0.05	0.0499984	$1.57e^{-7}$
6	0.11	0.1099935	$6.47e^{-6}$
7	0.06	0.0600106	$1.063e^{-5}$
8	0.21	0.2099707	$2.927e^{-5}$
9	0.19	0.1899708	$2.917e^{-4}$
10	0.22	0.2197351	$2.649e^{-4}$
NaCl + SL			
1	-0.47	-0.47	$1e^{-9}$
2	0.06	0.06	$3.e^{-9}$

3	0.09	0.09	$7.e^{-9}$
4	0.09	0.0900001	$6.3e^{-8}$
5	0.12	0.1199999	$6.7e^{-8}$
6	0.15	0.149999	$9.97e^{-7}$
7	0.17	0.1700002	$1.73e^{-7}$
8	0.23	0.2299978	$2.157e^{-6}$
9	0.25	0.2499896	$1.039e^{-5}$
10	0.28	0.2799955	$4.517e^{-6}$

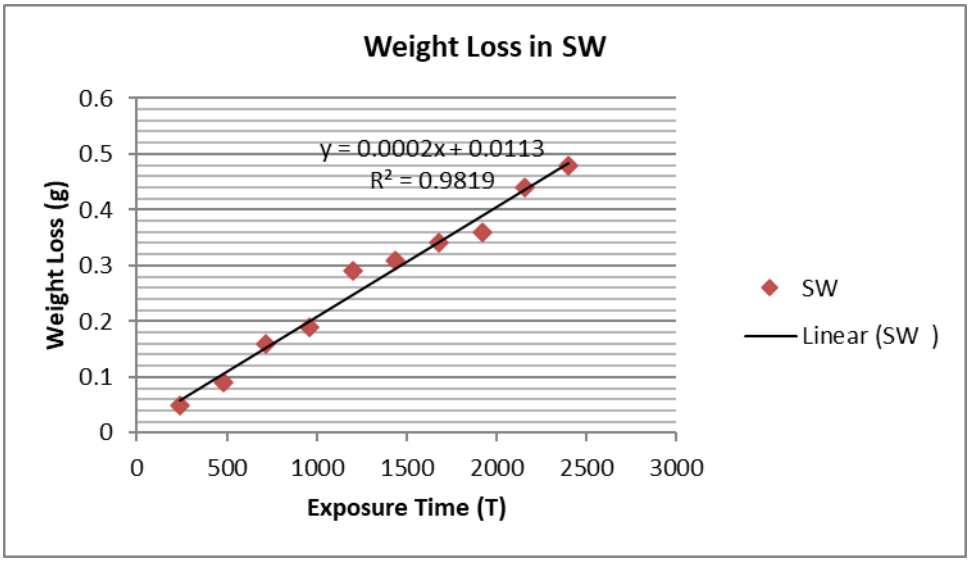


Figure 1 Weight Loss of Seawater

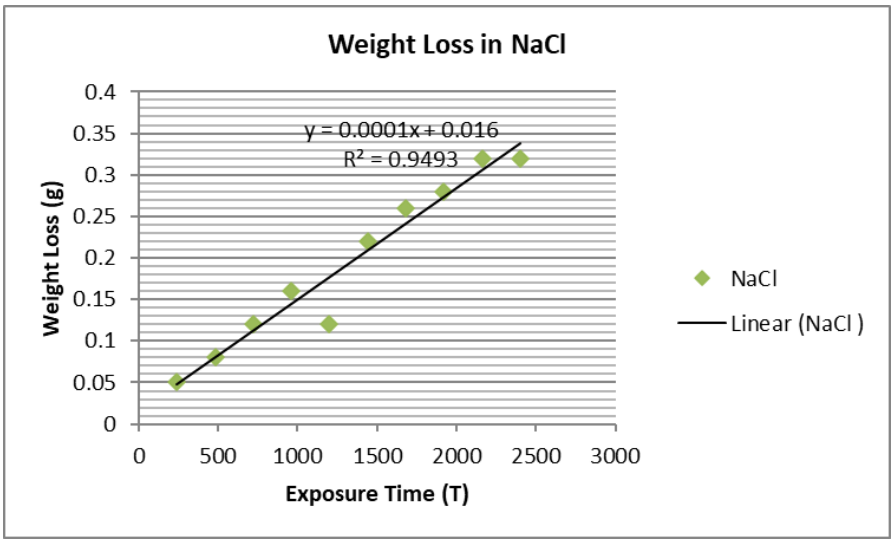


Figure 2 Weight Loss of Sodium Chloride

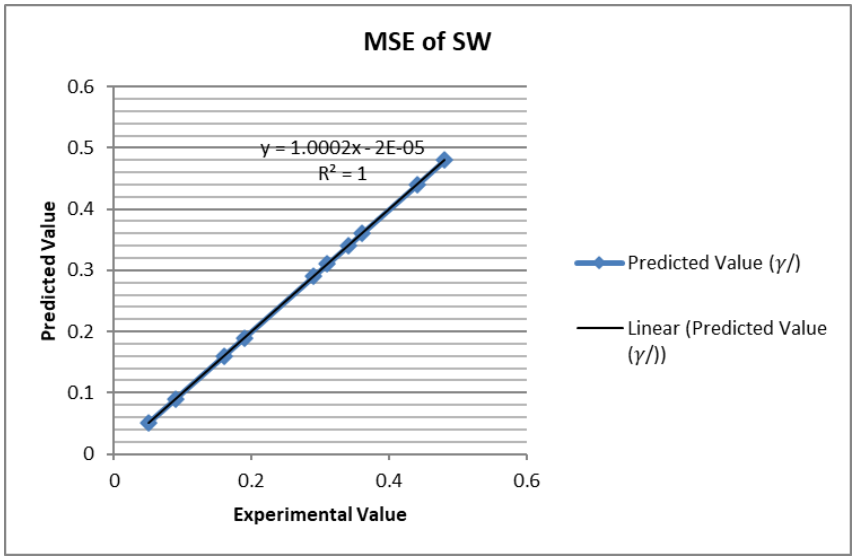


Figure 3 Prediction on Mean Square Error (MSE) of Seawater

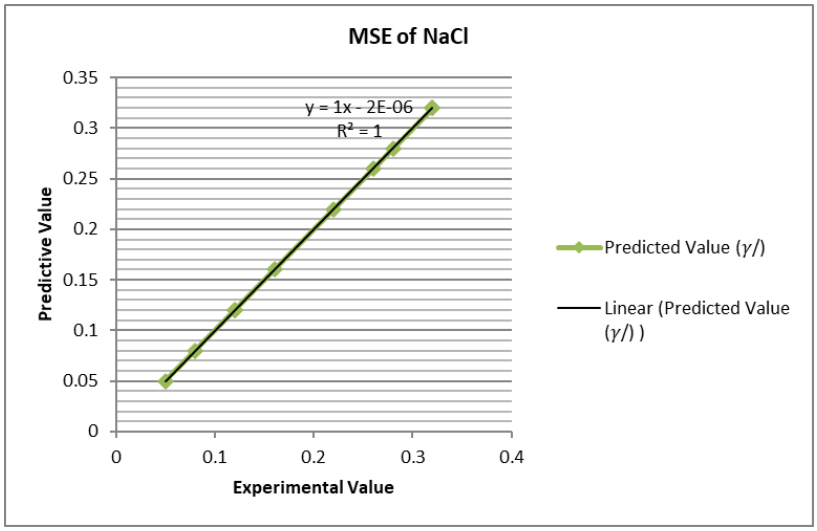


Figure 4 Prediction on Mean Square Error (MSE) of Sodium Chloride

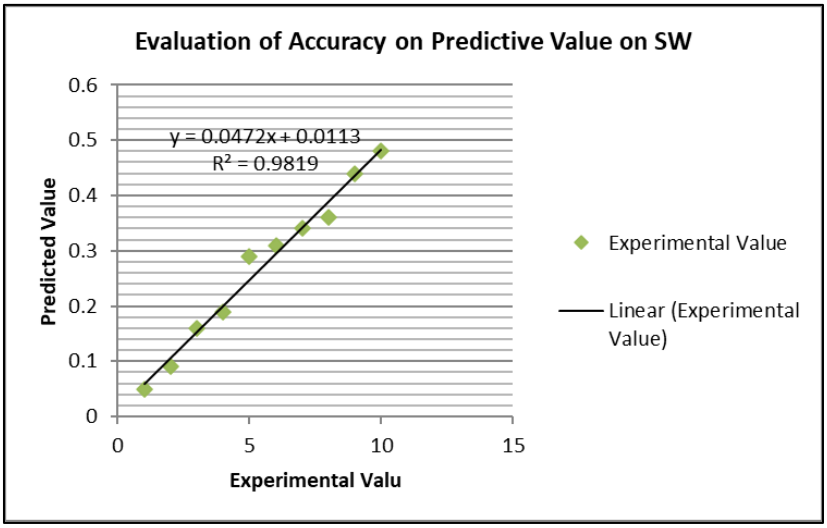


Figure 5 Prediction on Evaluation of Accuracy on Seawater

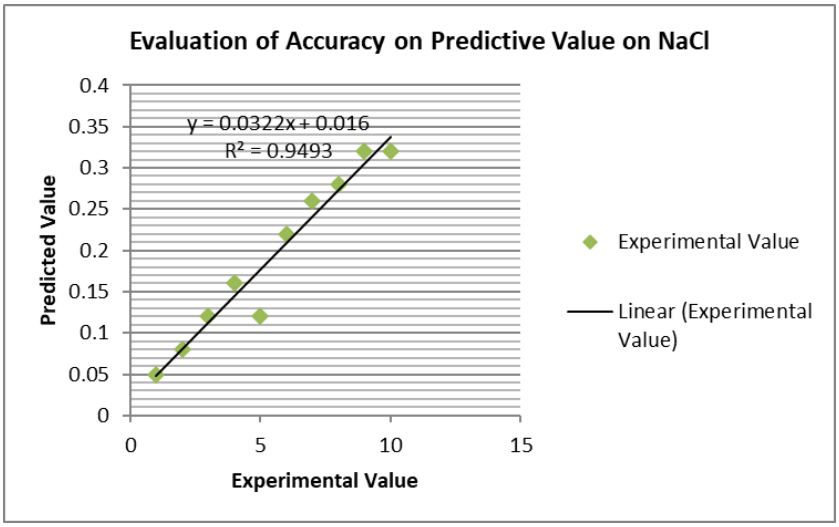


Figure 6 Prediction on Evaluation of Accuracy on Sodium Chloride

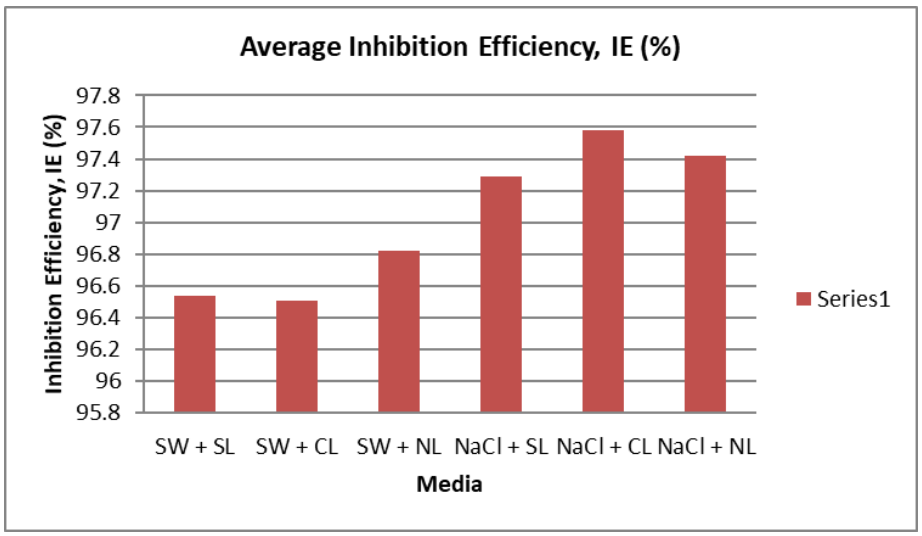


Figure 7 Inhibition Efficiency of Corrosion Inhibitors on Mild Steel C-1026 in different Corrosive Media

4. Discussion

From Table 1, the experimental data are shown. Seawater had higher weight loss than Sodium Chloride medium. The Seawater higher value of weight loss as compared with Sodium Chloride is probably because of the complex ionic composition of Seawater, presence of dissolved oxygen, pH and buffing capacity, and synergistic effects of multiple ions (Melchers. 2003; Little et al, 2007; Mansfeld. 1995). The values obtained from Table 2 shows that when Scent Leaf was added to Seawater, the weight loss was reduced from0.271 to 0.093, 0.064 and 0.022 respectively which might be attributed to formation of film on the metal surface.

Table 2 show the results of the corrosive media and the green plant inhibitors. It was observed that when Scent Leaf extract was added to Seawater and Sodium Chloride, Seawater had 0.093, while Sodium Chloride had 0.148 weight loss. In addition of Cassava Leaf, CL to the Seawater and Sodium Chloride, Seawater had 0.064; then Sodium Chloride had 0.083 weight losses. Also, when Neem Leaf was added to Seawater and Sodium Chloride, the weight loss of Seawater was 0.022, Sodium Chloride was 0.086. When the green plant inhibitors were added to the corrosive media, the weight losses on Sodium Chloride was more than the Seawater. This contradicted the claim of Seawater having greater weight loss than Sodium Chloride without inhibitors. This is due to according to Adekeye et al, (2020); Singh and Upadhyay (2008); Rastogi et al, (2002) that Sodium Chloride have higher osmotic gradient or dehydration, efficient semipermeable membrane action and empirical evidence as against Seawater. By higher osmotic gradient, it means that

NaCl is more hypertonic than Seawater which creates a stronger osmotic gradient. Moreover, the addition of the green plant extracts exhibited some corrosion inhibition efficiency as shown in

Table 3 and Fig. 5 show that Neem Leaf extract proved to be more efficient in Seawater environment with 96.82%. The efficiency of the Neem leaf extract might be due to its rich phytochemical composition, its effective adsorption onto metal surfaces and its protective barrier formation ability to mitigate corrosion in saline environments (Tuaweri et al, 2015). In NaCl, Cassava Leaf extract was observed to be more efficient with 97.58% against Neem Leaf with 97.42%. This can be ascribed to some specific chemical compositions (rutin flavonoid) in the Cassava leaves and the nature of interaction of the solution with the surface during the experimental hence the inhibition is measured (Abd El Rehim et al, 2010; Gusti et al, 2022; Ebuchi et al,2005; Gusti et al, 2016; Gusti et al,2017). The inhibition efficiency of Cassava Leaf extract has been observed in various conditions, both in stagnant and hydrodynamic environments. For instance, according to Charlet (2015), a concentration that contains 800 ppm of cassava leaf exhibited a corrosion inhibition efficiency of 97.4% at 35°C in stagnant condition.

Table 4 and 5 show the experimental and predictive values on Mean Square Error. It revealed that the error increases with increase in exposure time, and the experimental and predictive values on Weight loss observed at 100 days in Seawater were 0.48 and 0.048008474 with an error of 0.0008474, while the MSE experimental value and predictive value on Weight loss in Sodium Chloride were 0.32 and 0.32007343 with error of 0.0007343 respectively. The Seawater has higher error than Sodium Chloride due to the greater environmental complexity and variability of the Seawater (Melchers. 2003). According to Melchers (2003), Seawater has multiple ions such as Mg^{2+}, Ca^{2+}, SO^{2-}, K^{+} and HCO_3^{-}; organic matter, dissolved gases and microorganisms, while Sodium Chloride has only Na^{+} and Cl^{-} ions. The complexity properties of Seawater contributed to the greater weight loss and error (Melchers. 2003).

Table 6 and 7 show evaluation of accuracy on prediction of weight loss in Seawater and Sodium Chloride media disclosed that Seawater has both the experimental and predicted values to be 0.48 and 0.48008474, and Sodium Chloride has 0.32 and 0.32007343 with errors of 0.0008474 of Seawater and 0.00007343 of Sodium Chloride. This greater error value might be also attributed to the diverse ionic and physical properties of Seawater (Charlet. 2015).

Fig. 3 and Fig. 4 shows that y = 1.000x – 2E–05 and y = 1x - 2E-06, while $R^2 = 1$. The $R^2 = 1$ indicates that a perfect fit is established between the model and the experimental data, with all variability in the experimental values explained by the predictive model. According to Armstrong (2001), a perfect fit between the model and the data means that the predictive model exactly predicts the experimental values with zero error. Neter et al, (1996) stated that R^2 value of 1 explains that the model's predictions are exactly equivalent with the experimental values. While y = 1.000x – 2E–05 equations show a nearly perfect relationship between the experimental and predictive values, with a slope close to 1 and a very small intercept.

Fig. 5 and Fig. 6 shows that y = 0.047x+0.011 and y = 0.032x – 0.028, $R^2 = 0.981$ and $R^2 = 0.949$ respectively. The equations indicate that a weaker relationship is observed between the experimental and predictive values with a slope much less than 1. Moreso, the R^2 values of 0.981 and 0.949 suggest a good and strong fit between the model and the experimental data. $R^2 = 0.981$ and $R^2 = 0.949$ suggest good and strong fit because the model predicts outcome variables with some differences observed and the variables were close to 1 e.g. 0.9, 0.98. However, the good and strong fit has some variability in the experimental values which were not explained by the predictive model. They were not explained because there were some residuals that the model could not capture. Hastie et al, (2009) stated that a strong fit means the predictive model specifically predicts the experimental values with a small amount of error. Then according to Kvalseth (1985), the model explains a large proportion of variability in the experimental data which is seldom indicated by an R^2 value close to 1 (e.g., 0.9 or higher).

5. Conclusion

Maple Software was the statistic tool introduced to access the effectiveness of Scent Leaf, Cassava Leaf and Neem Leaf extracts as corrosion inhibitors on Mild Steel in the acidic media. From the investigation, it was observed that the inhibition efficiency and the various predictive models results were mainly influenced by the secondary metabolic properties in the plant extracts. Moreover, the concentration effect of the inhibitors was investigated and weight loss method was used to evaluate the efficiency of the corrosion inhibitors. The investigation revealed that the various green plant extracts exhibited good corrosion inhibition efficiencies in the different corrosive media. Furthermore, the investigation revealed that the predicted values gave minimal errors and were closer to the experimental values in Mathematical Model.

Compliance with ethical standards

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Disclosure of conflict of interest

No conflict of interest to be disclosed.

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