Joires 6(1), March, 2025.
ISSN: 2141-8217.
https://journals.unizik.edu.ng/joires/about

Multi-Factorial Prediction of Mild Steel Exposure Time during Its Corrosion Inhibitionwith Hibiscus Sabdariffa Leaf Extract in 0.5M H_2SO_4

(pp. 652-665)

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Abstract: This paper evaluates the exposure time of mild steel (which corroded in sulphur acid solution while in contact with an inhibitor- Hibiscus Sabdriffa) based on pre-determined penetration depth and corrosion rate. The analysis carried out was using a derived empirical model; $\theta = \exp(\text{ꞗ}(\delta\gamma\xi^{-1}) - \text{ß})$. Mild steel was submerged in 0.5M H_2SO_4 containing sabdariffa leaf extract which serves to inhibit corrosion of the steel. In the course of the model derivation, following experimentals, the applied range of values of the process parameters: exposure time, penetration depth and corrosion rate were 0.00548 – 0.011 hrs, 0.0047 – 1.0121mm, 0.8638-0.1027mm/yr respectively. The validity of the model is strongly rooted on the core model structure; $\ln\theta + \text{ß} \approx \text{ꞗ}(\delta\gamma\xi^{-1})$. The model-predicted results agree with previous research on the direct relationship between the corrosion rate & penetration rate and exposure time, while inhibitor concentration is constant. The standard error incurred in predicting the model based exposure time relative to the experimental results was 0.0004%, implying over 99% model confidence level. The exposure times per unit penetration depth and corrosion rate for experimental & model-predicted results were evaluated as: 0.7459 & 0.9297 yr mm^{-1} and 0.0231 & 0.0288 $(yr)^2$ mm^{-1} respectively. Furthermore, the correlations between these highlighted parameters, as evaluated from both results were all > 0.97. The overall maximum deviation of model-predicted mild steel exposure time from experimental results was 9.09%.

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Keywords: Exposure time prediction, mild steel, corrosion inhibition, hibiscus sabdariffa leaf extract, sulphuric acid.

INTRODUCTION

Thorough investigation revealed that no existing mathematical expression shows what happens to the mild steel, while the exposure time increases and inhibitor (Hibiscus Sabdariffa) concentration is constant. This therefore raised the need for the present work to fill in the gap. A researcher Agu (2023) has shown corrosion as a natural process which alters the physicochemical properties of a metal or alloy as a result of its reaction with its immediate environment. The corrosion process converts a refined metal or alloy which is in a metastable energy state to a more stable low energy state in the form of oxides or hydroxides in which forms the metal or alloy existed before their refining. The corrosion reaction facilitates the return of the metal or alloy to those original compounds. These reactions take place when metals or alloys are exposed in the air, in solutions or buried in the ground. The process degrades the physical, chemical, electrical properties of the metals or alloys. The corrosion on the metal components can be localized to form a pit or crack or can be uniformly experienced on the corroding surface. It is essentially an electrochemical process and it causes a lot of damage to assets and property, injury to people and loss of time and other resources in the industry.

Corrosion leads to loss of man-hours, unscheduled shutdown, component maintenance and replacement costs etc. In fact, a team of scientists (Akinyemi et al, 2012) has shown that corrosion is the single largest cause of plant and equipment breakdown in the Oil and Gas industries. The World Corrosion Organization also posited that the annual cost of corrosion globally is approximately 2.2 trillion US dollars. This represents over 3% of world's Gross Domestic Product (GDP) (Kochi et al.2002). Corrosion control, as a result, becomes imperative and no level or amount of resources and technologies invested in corrosion control is wasted.

Approaches to corrosion control include but not limited to materials selection, design, cathodic protection, coating, galvanic protection, and inhibition. Inhibition approach uses inhibitors to retard either the anodic or cathodic reaction in a corrosion process or both. Inhibitors are of two major types, namely, organic and inorganic inhibitors. Inorganic inhibitors as well as some of the available corrosion control technologies and approaches are expensive, toxic/harmful to the environment and not bio-degradable thus causing more nuisance in the ecosystem while organic inhibitors offset these shortcomings.Nature, luckily, has provided the source/raw materials for organic inhibitors through leaves and herbs. Some of these extracts (Shahen et al., 2022, Nguyen et al., 2018, Amabuo, 2024) have shown remarkable retardation in mild steel corrosion. These materials are available, non-toxic mostly, biodegradable unlike the inorganic inhibitors and other corrosion control materials and approaches.

Nwoye (2020) has shown that the corrosion current density $\acute{\imath}_{corr}$ is a function of the concentration ϑ and inhibition efficiency η of hydroxypropyl cellulose (inhibitor), having been discovered to resists corrosion of aluminum in hydrochloric acid solution. The response analysis was carried out within a range of process parameter; 18.35-30.11(μAcm^{-2}), 1-5 (g/l) and 74.22-84.29 (%) for current densities, inhibitor concentrations and inhibition efficiencies respectively. The investigation prompted the derivation of an empirical model;

$$\acute{\imath}_{corr} = -0.58\eta - 1.43\vartheta + 74.35 \qquad (1)$$

which predicted the response of the corrosion current density as sum of two linear parts, involving inhibition efficiency and inhibitor concentration. Results predicted by the Derived Response Model (DRM) show that the current density decreases with increase in both inhibitor concentration and efficiency. The decrease in the corrosion current density basically implies reduction in corrosion attack on the aluminium. The validity of the model was rooted on the core model expression $\acute{\imath}_{corr} - K = -\text{Ϧ}\eta - N\vartheta$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based current density relative to the actual results was 0.48%.

Following the research outcome, evaluations from generated results indicated that the corrosion current density per unit inhibitor concentration as obtained from the actual and model-predicted results are 2.94 and 2.89 (μAcm^{-2})/(g/l) respectively. Maximum deviation of model-predicted results (from actual results) was < 3.2%. This translates into over 96% operational confidence levels for the derived model and 0.96 dependency coefficient of the current density on inhibition efficiency and inhibitor concentration. The correlation coefficients between values of current density and inhibition efficiency & inhibitor concentration from model-predicted results were all > 98%.

Hibiscus Sadariffahas been successfully used (Agu, 2023) as a viable inhibitor to resists corrosion of mild steel in sulphuric acid solution. The research showed that the corrosion rate of mild steel in the sulphuric acid solution decreased and increased with the inhibitor concentration and exposure time respectively.

The present work aims at predicting the exposure time based on the pre-determined corrosion rate and penetration depth, within the period mild steel was submerged in sulphuric acid solution (in contact with Hibiscus Sabdariffa as inhibitor). It is strongly believed that the model if derived will predict within the range of experimental range of values, the time within which the mild steel serving in sulphuric acid solution. This follows substitution into the model, values of the corrosion rate and its penetration depth, providing the boundary conditions are considered.

2. Materials and methods

Gravimetric (weight loss) approach was used to evaluate the inhibition performance of HS in the acidic medium; 0.5M, H_2SO_4

2.1 Gravimetric Analysis

The gravimetric (weight loss) method is the most widely method of corrosion inhibition assessment (Musa et al., 2010). In this study, the mild steel coupons were mechanically press-cut into dimensions of 40mm×30mm×20mm with a hole 1.5mm diameter at the top centre of the coupon. They were cleaned with energy paper of increasing mesh size until mirror surface and kept in a desicator. The leaves of Hibiscus Sabdariffa were sun-dried and a mass of 200g was soaked in one litre of ethanol for 48hrs. The filtrate (containing inhibitor and ethanol) was decanted into a conical flask and the residue, after extracting the liquid, was discarded. The filtrate was allowed open with mild heating for ethanol to evaporate at 78°C. The 0.5m H_2SO_4. The weighing was done with the 4-digit HAUS electronic weighing machine

Corrosion rate, expressed in mm/yr, was determined by

$$\xi = \frac{k\Delta W}{\rho A t} \qquad (2)$$

where,

A = Exposed surface area; $2(LB+LT+BT) - 2(\pi\frac{d^2}{4}) + \pi dT$ (mm^2)

L, B, T and D are length, breadth, thickness and diameter (mm) respectively

ρ = Density of the mild steel ($7.85 g/cm^3$).

t = θ; Exposure time (year)

k = constant; 8.76×10^4 (for corrosion rate in mm/yr)

ΔW = Weight loss following corrosion (g)

The efficiency of the inhibitor (%) used was evaluated using the expression;

$$\eta = \left(\frac{C_a - C_i}{C_a}\right) \times 100\% \qquad (3)$$

Corrosion penetration depth δ (mm) is calculated using the expression;

$$\delta = \theta\, C_i \qquad (4)$$

where,

C_a = Corrosion rate in absence of inhibitor (mm/yr)

C_i= Corrosion rate in presence of inhibitor (mm/yr)

Table 1: Variation of exposure time with mild steel corrosion rate and penetration depth at constant inhibitor concentration (Agu, 2023)

(θ)	(θ)	(ξ)	(δ)	(γ)
48	0.00548	0.8638	0.0047	5.0
60	0.00685	0.9469	0.0065	5.0
72	0.00822	1.0300	0.0085	5.0
84	0.00959	1.0664	0.0100	5.0
96	0.0110	1.1027	0.0121	5.0

Model Formulation

Computational analysis of the experimental results shown in Table 1, resulted to Table 2 which indicate that;

$$\ln\theta + ß \approx ђ(\delta\gamma/\xi) \qquad (5)$$

$$\ln\theta = ђ(\delta\gamma/\xi) - ß(\qquad (6)$$

$$\theta = \exp\left(\frac{ђ\delta\gamma}{\xi} - ß\right) \qquad (7)$$

The derived model shown as a mathematical expression in (7) predicts the exposure time within which mild steel corroded (even under protection by inhibitor) while submerged in H_2SO_4. The variables θ, δ, γ and ξ are exposure time (yr), penetration depth (mm), concentration of inhibitor and corrosion rate (mm/yr) respectively. The equalizing constants; ђ and ß are 31.25 and 6.125 respectively. The constants were generated using a software (Nwoye, 2008). The interaction between these constants and variables ensures that the units at both sides of the derived model are equal.

4. Results and Discussion

4.1 Boundary and Initial Conditions

Consider mild steel, interacting with sulphuric acid in the presence of sabdariffa (inhibitor). Corrosion of the mild steel was determined by the roles played by the sulphuric acid and inhibitor. The extents of the roles by these aqueous solutions were in turn dependent of their various concentrations. During the model derivation, the considered ranges of exposure time, penetration depth and corrosion rate were 0.00548 – 0.011 hrs, 0.0047 – 1.0121mm, 0.8638-0.1027mm/yr respectively.

Table 2: Variation of lnθ + ß with Ђ (δγ ⁄ ξ)

lnθ + ß	Ђ (δγ ⁄ ξ)	Differential
0.9183	0.8502	0.0681
1.1415	1.0726	0.0689
1.3238	1.2894	0.0344
1.4780	1.4652	0.0128
1.6151	1.7145	-0.0994

4.2 Model Validity

The derived model was also validated by comparing the predicted results with the experimental, through graphical, statistical and deviational analysis.

4.2.1 Graphical Analysis

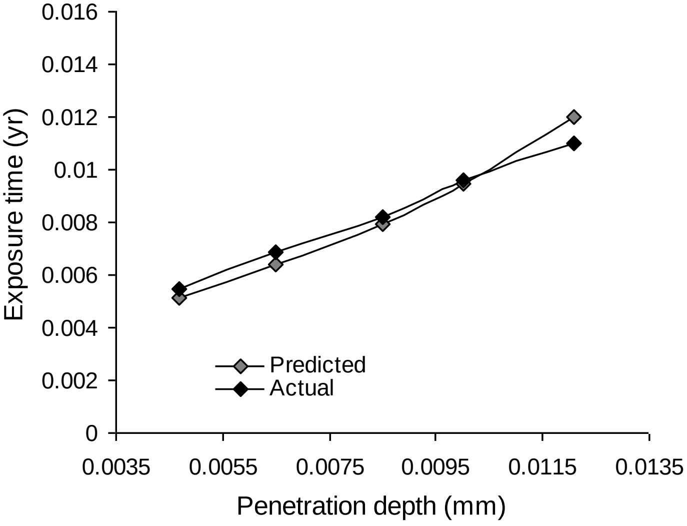

Fig. 1: Variation of corrosion penetration depth with exposure timeas obtained from experiment and model prediction

Table 1 shows the variation of corrosion rates and depth penetration with the exposure time of the steel in the acid solution. The core model structure expressed in (1) is the basis on which the validity of the model in (7) is rooted. This is hinged on the fact that the evaluated structure components at both sides of the structure are correspondingly almost equal as shown in Table 2. The negligible differentials recorded in each line of Table 2 shows that both sides of the model components are correspondingly almost equal. This indicates that any variable evaluated as subject formular will likely be precise with very admissible deviation.

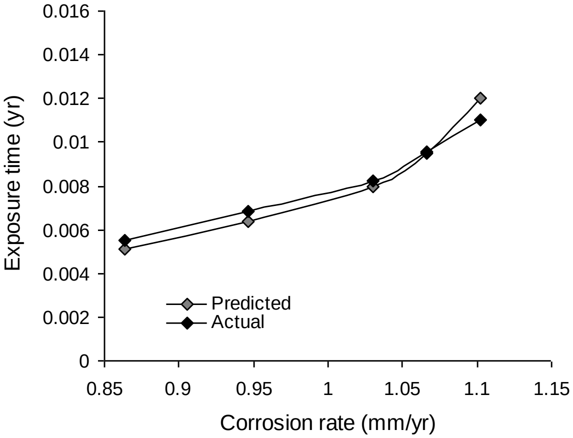

Fig. 2: Variation of corrosion rate with exposure timeas obtained from experiment and model prediction

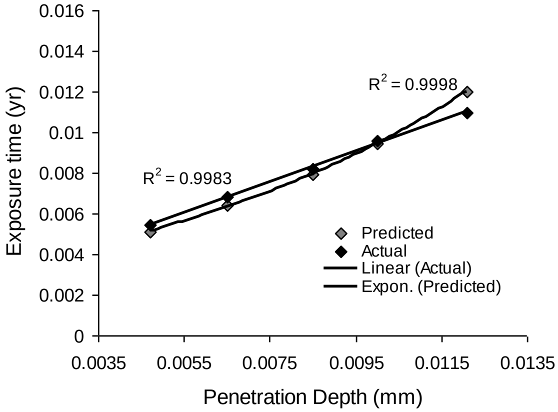

Figure 3: Comparison of mild steel exposure times(relative to penetration depths) as evaluated from experimental results and derived model

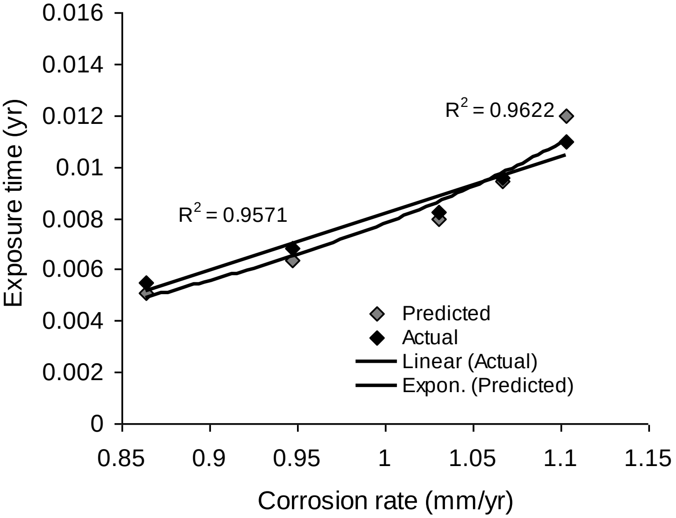

Figure 4: Comparison of mild steel exposure times(relative to corrosion rate) as evaluated from experimental results and derived model

Results generated from experimental and model-predictedresults in Figs. 1 & 2 and Figs. 3 & 4 are same in all ramifications except that the later shows the correlations between the exposure time and penetration depth and corrosion rate. On the other hand, curves of experimental, model-predicted and regression results, represented by the mild steel exposure times, relative to penetration depth and corrosion rate are shown in Figure 5 and Figure 6 respectively. These figures are characterized by similar trend and spread of results point distribution. The exposure times plotted in these figures show direct relationships with penetration depth and corrosion rate, and so emphasize positive slopes respectively.

The essence of the regression analysis is to verify the trend and spread of results shown by the derived model predictions with respect to the experimental results. The level of alignment of the three curves indicates the degree of acceptability admissibility of the derived model.

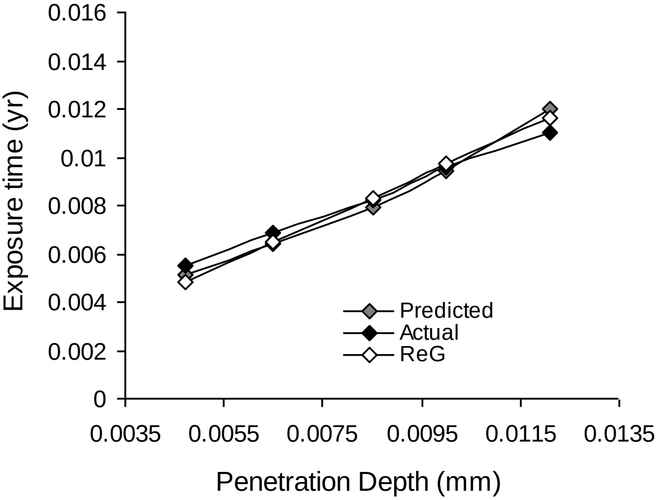

Figure 5:Comparison of mild steel exposure times(relative to penetration depths) as evaluated from experiment, derived model and regression model

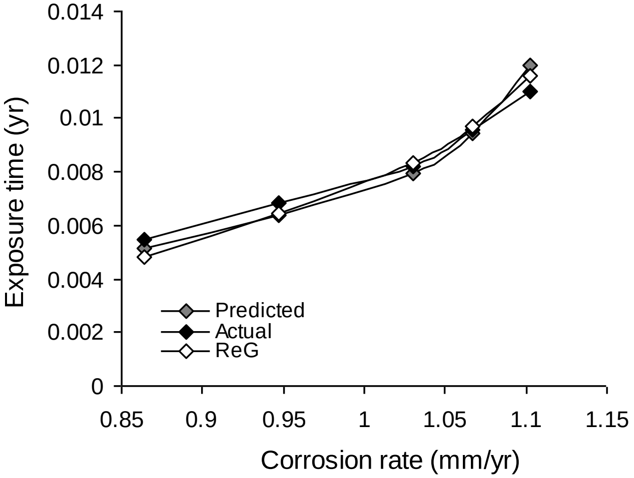

Figure 6: Comparison of mild steel exposure times(relative to corrosion rates) as evaluated from experiment, derived model and regression model

4.2.2 StatisticalAnalysis

Correlations evaluated (using Microsoft Excel version 2003) from the coefficients of determination R^2 shown in Figure 3 and Figure 4, between exposure time and penetration depth & corrosion rate are 0.9991 and 0.9999 & 0.9783 and 0.9809, using experimental results and model predictions respectively. Comparative analyses of these correlations indicate a better line fittedness with penetration depth.The correlations were calculated using the relationship

$$R = \sqrt{R^2} \qquad (8)$$

For every change in the corrosion rate and penetration depth, analysis of the overall standard error incurred on predicting the exposure time, relative to experimental results revealed a value equal 0.0004%. This gives a model confidence level above 99.9%. The standard error was evaluated using Microsoft Excel version 2003.

Table 3: Differential between experimentally determined andmodel-predicted mild steel exposure times

(θ)	$\Delta\theta = \theta_M - \theta_\varepsilon$
0.00548	- 0.00036
0.00685	- 0.00047
0.00822	- 0.00027
0.00959	- 0.00012
0.0110	- 0.001

Table 3 outlines negligible differentials between experimentally determined and corresponding model-predicted exposure times. This shows to a significant level that the derived model is functional and admissible. The table also shows that these differentials have positive and negative values, relative to the corresponding experimental results. This indicates increased and decreased model-predicted values respectively.

4.2.3 Deviational Analysis

Analysis of exposure times as obtained from actual and derived model show deviation of model-predicted values from those of the actual. This is believed to be due to the fact that some considered assumptions and experiment-oriented conditions which prevailed during the actual field work were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted values to those of the actual.

Deviation (Dv) (%) of the model-predicted exposure time from that of the experimental is given by

$$Dv = \frac{\theta_m - \theta_E}{\theta_a} \times 100 \qquad (9)$$

where
θ_m= Model-predicted exposure time
θ_a= Exposure time evaluated from experimental results

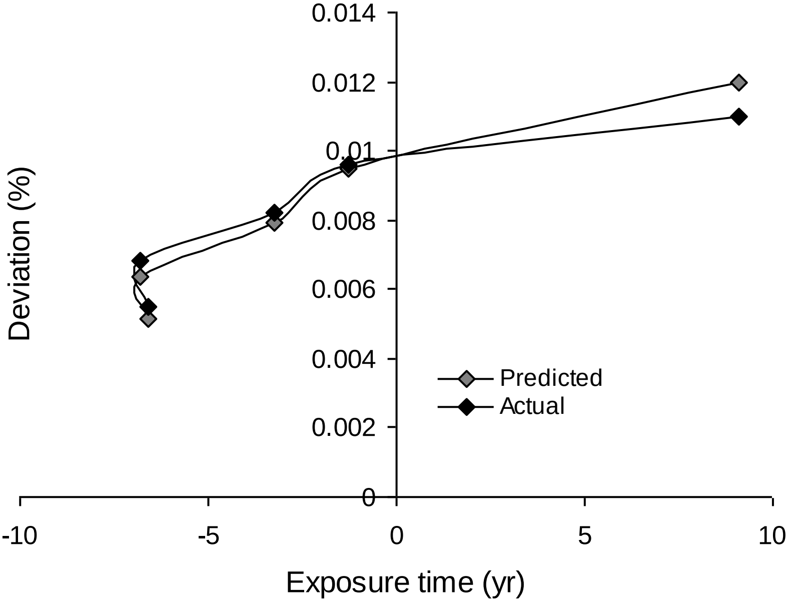

Figure 7: Variation of model-predicted exposure time with its corresponding deviation from experimental results

The deviation of model-predicted exposure time from corresponding experimental results is shown in Figure 7. The figure indicates that the overall maximum deviation of model-predicted θ is 9.09%. This gives operational model confidence levels above 90%. It is also shown that the least and highest magnitude of deviations of the model-predicted θ is – 1.27 and 9.09% respectively. Invariably these deviations correspond to the corrosion penetration rates: 0.01 & 0.0121 mm and corrosion rates: 1.0664 & 1.1027mm/yr respectively. Following series of highlighted evaluations, the overall model confidence level places between 90 and 99%.

Correction factor (Cr) is the negative of the deviation i.e

$$\mathrm{Cr} = -\mathrm{Dv} \qquad (10)$$

Therefore

$$\mathrm{Cr} = -100 \left[\frac{\theta_m - \theta_a}{\theta_a}\right] \qquad (11)$$

Introduction of the corresponding values of Cf from equation (11) into the model gives exactly the corresponding experimental values. Equations (10) and (11) show that correction factor is the negative of the deviation. It is strongly believed that the correction factor takes care of the assumptions made and experimental condition prevailing during the field works which were not considered during the model formulation.

The deviation of model predicted results from that of the experimental is just the magnitude of the value. The associated sign preceding the value signifies that the deviation is deficit (negative sign) or surplus (positive sign). Mild steel exposure time per unit corrosion penetration depth E_δ (θ/δ) yr (mm)$^{-1}$was calculated from the expression;

$$E_\delta = \frac{\theta}{\delta} \qquad (12)$$

Re-written as

$$E_\delta = \frac{\Delta\theta}{\Delta\delta} \qquad (13)$$

The expression (13), is detailed as

$$E_\delta = \frac{\theta_2 - \theta_1}{\delta_2 - \delta_1} \qquad (14)$$

where

ΔE = Change in the mild steel exposure times θ_2, θ_1 at two
Penetration depths δ_2, δ_1

Plotting points (0.0047, 0.00548) & (0.0121, 0.011) and (0.0047, 0.00512) & (0.0121, 0.012) as shown in Figure 1, designated as (δ_1, θ_1) and (δ_2, θ_2) for experimental and model-predicted results, and then substituting them into the expression (14), gives the slopes: 0.7459 and 0.9297 yr mm^{-1}, as their respective exposure times per unit penetration depth. Mild steel exposure time per unit corrosion rate E_ξ (θ/ξ) yr^2(mm)$^{-1}$was calculated from the expression;

$$E_\xi = \frac{E}{\xi} \qquad (15)$$

Re-written as

$$E_{\xi} = \frac{\Delta E}{\Delta \xi} \qquad (16)$$

The expression (16), is detailed as

$$E_{\xi} = \frac{E_2 - E_1}{\xi_2 - \xi_1} \qquad (17)$$

where

$\Delta\xi$ = Change in the corrosion rates ξ_2, ξ_1

Plotting points (0.8638, 0.00548) & (1.1027, 0.011) and (0.0047, 0.00512) & (0.0121, 0.012) as shown in Figure 2, designated as (δ_1, ξ_1) and (δ_2, ξ_2) for experimental and model-predicted results, and then substituting them into the expression (17), gives the slopes: 0.0231 and 0.0288 $(\text{yr})^2\ \text{mm}^{-1}$, as their respective exposure times per unit corrosion rate.

5. Conclusion

The exposure time of mild steel (which corroded in sulphur acid solution while in contact with an indicator- Hibiscus Sabdriffa) has been predicted based on pre-determined penetration depth and corrosion rate. An empirical model; $\theta = \exp(\text{ɧ}(\delta\gamma\xi^{-1}) - \text{ß})$ was derived, validated and used for the analysis. The validity of the model is strongly rooted on the core model structure; $\ln\theta + \text{ß} \approx \text{ɧ}\ (\delta\gamma\xi^{-1})$. There is a direct relationship between the corrosion rate & penetration rate and exposure time, while inhibitor concentration is constant. The standard error incurred in predicting the model-based exposure time relative to the experimental results was 0.0004%, implying over 99% model confidence level. The exposure times per unit penetration depth and corrosion rate for experimental & model-predicted results were evaluated as: 0.7459 & 0.9297 yr mm^{-1} and 0.0231 & 0.0288 $(\text{yr})^2\ \text{mm}^{-1}$ respectively. The correlations between these highlighted parameters, as evaluated from both results were all > 0.97. The overall maximum deviation of model-predicted mild steel exposure time from experimental results was 9.09%. The limitation of this work is that the mild steel exposure time cannot be predicted beyond the boundary conditions except through simulation.

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