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Predictive Analysis of Mild Steel Corrosion Rate during Inhibitive Activities of Chicken Nail Extracts in 2M Sulphuric Acid Solution

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Abstract
This paper presents the predictive analysis of mild steel corrosion rate during the inhibitive activities of Chicken nail extract in 2M sulphuric acid. The range of process parameters used for reaction temperatures, corrosion rates, inhibitor concentrations and exposure times are 45- 70 (^{0}C), 1.216- 4.422 (mg /mm^2 h), 0.67-1.5 (g/l) and 5.5-8 (hrs) respectively. The mild steel corrosion rate was evaluated to be a direct function of the sum of the natural logarithms of reaction temperatures, inhibitor concentrations and exposure times. An empirical model; $\text{ђ} = 1.3567 \ln \vartheta + 2.6196 \ln \beta + 3.1095 \ln \varepsilon - 13.49$ predicts the corrosion rate with maximum deviation < 9.85% (from actual results). This translated into over 91.15% operational confidence levels for the derived model. The validity of the model was rooted on the core model expression $\text{ђ} + K = N \ln \vartheta + S \ln \beta + S_e \ln \varepsilon$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based corrosion rate relative to values of the actual results is 0.2258. The correlation coefficients between corrosion rate and reaction temperature, inhibitor concentration and exposure time were all > 0.97.

Keywords: Mild steel corrosion, Chicken nail extract, sulphuric acid.

1. Introduction

Mild steel has remained till date the most widely used ferrous alloy for a broad spectrum of applications. This is attributed to its weldability during construction of steel structures. Corrosion inhibition involves a process of suppressing or reducing corrosion. This has been adduced [Palou et al., 2014; Evrim et al., 2016] to be the most economical and practical approach to reducing corrosion attack on metals and alloys. Very scintillating results [Olawale et al., 2015; Olawale et al., 2018; Ita et al., 2016; Li et al., 2014; Omotioma et al., 2017; Anadebe et al., 2018; Fouda et al., 2016; Udunwa et al., 2017; Chidiebere et al., 2016] have been generated by using various plant extracts for corrosion inhibition. Some of these plants includes; Bitter kola leaf, Ocimum gratissium, Gentiana olivieri, Cashew waste, Katemfe Bamboo, Pawpaw leaves and Thevetia Peruvianna, Delonixregia. Investigation [Oguzie et al., 2014] has been carried out on the inhibition efficacy of aqueous extracts of the leaves of *Delonixregia* (DR) in 1 M HCl and 0.5 M H_2SO_4 using weight loss, electrochemical and surface probe techniques. Results of the investigation revealed that via adsorption of the extract organic matter on the metal/solution interface, DR extract inhibited mild steel corrosion in both acidic environments. Furthermore, Potentiodynamic polarization shows that DR is a mixed type inhibitor in both acidic environments, whereas the impedance results revealed adsorption of the DR species on a corroding steel surface. Also increase in inhibition efficiency was dependent on concentration. The adsorption of DR followed Langmuir adsorption isotherm. A protective layer was formed and adsorbed on a mild steel surface in the acid solutions as indicated in the result of Scanning electron microscopy (SEM). Report [Chidiebere et al., 2015] has shown that inhibitors whose adsorption process is stabilized at the reaction centers have polar functional groups. The group prompts up reduction in corrosion susceptibility of the metal surface and so the service life of the metal is prolonged. Chicken nails extract (CNE) has been successfully used for inhibiting mild steel corrosion in 2M H_2SO_4 [Olawale et al., 2019]. The effect of some process parameters such as the inhibitor concentration (0.5–1.5g/l), time (5–8h) and temperature (40-70^{0}C) on inhibition efficiency were investigated using Response Surface Methodology. The Physiochemical analysis and proximate analysis of the CNE were also investigated. The result of the investigation revealed presence of organic constituents which marked the Chicken nails extract as reliably inhibitor. The inhibition efficiency increased as the inhibitor concentration increased while the rate of corrosion increases as time and temperature increased. The optimum conditions obtained were inhibitor concentration of 0.1 g/l, time 5 h and temperature 63.63^{0}C. The optimum Inhibition Efficiency at these optimum conditions was 74.04%. Result of Scanning Electron Microscopy revealed presence of passive layer of a film formed on the surface as a result of presence of the inhibitor. Previous research [Olawale et al., 2019] investigated the effect of inhibitor derived from chicken nails, temperature and exposure time on the inhibition of mild steel corrosion rate. Based on the foregoing, there is need to express the corrosion rate of the steel, directly in terms of the highlighted parameters, other than the conventional techniques, which includes gravimetric or weight loss method [Olawale et al., 2019]. This will ensure precision in the corrosion rate of the steel, unlike in the case of weight loss method, where errors might be incurred during measurement of the weight of coupon and determination of the material`s density. The present work aims at predicting the corrosion rate of mild steel in sulphuric acid, using a derived empirical model, based on the chicken nail extract (inhibitor) concentration, exposure time and reaction temperature. This research is in furtherance to the previous work [Olawale et al., 2019], which dealt purely on experiment. It is strongly believed that the derived model will predict the mild steel corrosion rate within the actual range, on substituting into the model, values of the highlighted process parameters, providing the boundary conditions are considered.

2.0 Material and methods

2.1 Preparation of mild steel coupon

Mild Steel obtained from the Mechanical Engineering laboratory was cut into Coupons of dimension, thickness and middle-drilled hole diameter; 2cm by 2cm, 0.2 cm and 0.2 cm respectively, before cleaning with emery paper to expose the shiny surface, degreasing with acetone to remove any oil impurity, washing using distilled water and then drying in air before storing them in a desiccators [Olawale et al., 2019].

2.2 Preparation of chicken nails extract

The chicken nails (CN) used were collected from Landmark University Teaching and Research farm and dried for five (5) days. Dried CN was then pulverized and kept for extraction. For each extraction process conducted, 30 g of the chicken nails powder was placed in the Soxhlet extractor with 180 cm^3 of ethanol for 4 h. The extract solution was afterwards concentrated and employed for the preparation of inhibitors concentrations in 2M H_2SO_4. The Gravimetric or weight loss method of the corrosion inhibition study and other techniques used are as stated in the previous work [Olawale et al., 2019].

3.0 Results and Discussions

Table 1: Variation of corrosion rate ɧ of mild steel with concentration of inhibitor ϑ, exposure time ε and reaction temperature β [15].

(β)	(ε)	(ϑ)	(ɧ)
45	5.5	0.67	1.216
50	6.0	0.84	2.321
60	7.0	1.17	3.758
65	7.5	1.34	4.086

Computational analysis of the actual results shown in Table 1, gave rise to Table 2 which indicate that;

$$ɧ + K = N \ln \vartheta + S \ln \beta + S_e \ln \varepsilon \quad (1)$$

Introducing the values of K, N, S and S_e into equation (1) reduces it to;

$$ɧ = 1.3567 \ln \vartheta + 2.6196 \ln \beta + 3.1095 \ln \varepsilon - 13.49 \quad (2)$$

Where

K = 13.49, N = 1.3567, S = 2.6196 and S_e = 3.1095; equalizing constant (determined using C-NIKBRAN [Nwoye, 2016])

(ɧ) = Corrosion rate of mild steel in sulphuric acid solution (mg/mm^2 h)

(ϑ) = Concentration of inhibitor (g/l)

(ε) = Exposure time (hr)

(β) = Reaction temperature (^{0}C)

The triple natural logarithmic model predicts the mild steel corrosion rate at known inhibitor concentration, exposure time of the steel and reaction temperature.

3.1 Boundary and Initial Conditions

Consider short cylindrically shaped mild steel coupon submerged in H_2SO_4- chicken nail extract solution, interacting with some corrosion-induced agents. The solution is assumed to be affected by undesirable dissolved gases. The considered range of the reaction temperatures, corrosion rate, inhibitor concentrations and exposure times are 45- 70 (^{0}C),1.216 - 4.422 (mg/ mm^2 h), 0.67 - 1.5 (g/l) and 5.5 – 8 (hrs) respectively.

Table 2: Variation of Ђ + 13.49 with 1.3567 ln ϑ + 2.6196 ln β + 3.1095 ln ε

Ђ + 13.49	1.3567 ln ϑ + 2.6196 ln β + 3.1095 ln ε
14.7060	14.7295
15.8110	15.5829
17.2480	16.9893
17.5760	17.5976
17.9120	18.1455

3.2 Model Validation

The validity of the model is strongly rooted on the core model equation (1) where both sides of the equation are correspondingly almost equal. Table 2 also agrees with equation (1) following the values of Ђ + 13.49 and 1.3567 ln ϑ + 2.6196 ln β + 3.1095 ln ε evaluated from the actual results in Table 1. Furthermore, the derived model was validated by carrying out deviational analysis and statistical analysis, involving evaluation of the correlations and standard errors.

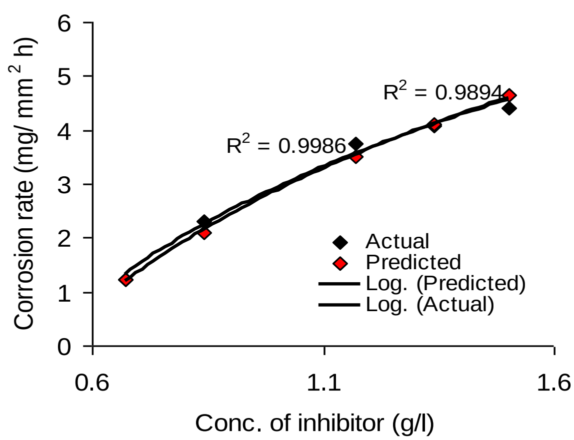

Fig.1: Coefficient of determination between corrosion rate and concentration of inhibitor as obtained from actual and model-predicted results.

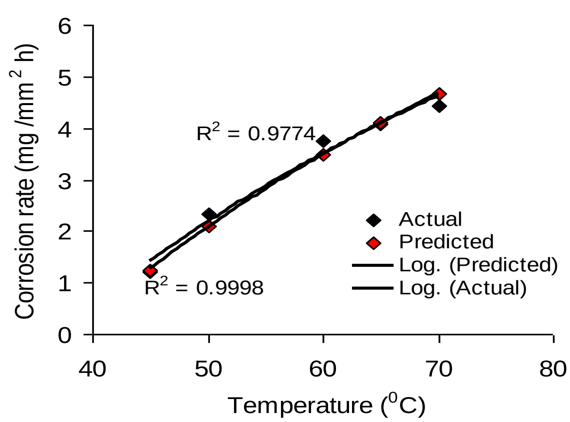

Fig.2: Coefficient of determination between corrosion rate and reaction temperature as obtained from actual and model-predicted results.

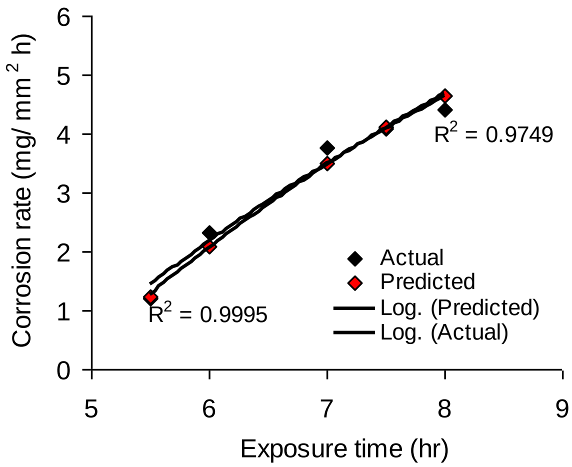

Fig.3: Coefficient of determination between corrosion rate and exposure time as obtained from actual and model-predicted results.

3.2.1 Statistical analysis

3.2.1.1 Correlation

The correlation coefficient between corrosion rate and concentration of inhibitor, reaction temperature & exposure time were evaluated (using Microsoft Excel Version 2003) from results of the actual and derived model. These results are 0.9993 and 0.9947, 0.9886 and 0.9999 & 0.9874 and 0.9997 respectively. The evaluations were based on the coefficients of determination R^2 shown in Figs. 1-3 and calculated using equation (3).

$$R = \sqrt{R^2} \tag{3}$$

3.2.1.2 Standard Error (STEYX)

The standard error incurred in predicting the model-based corrosion rate relative to values of the actual results is 0.2258. The standard error was evaluated using Microsoft Excel version 2003.

3.2.2 Graphical Analysis

Comparative analysis of Figs. 4-6 show curves and shapes perimeters of model-predicted and actual results with high degree of alignment. This indicates proximate agreement between both results.

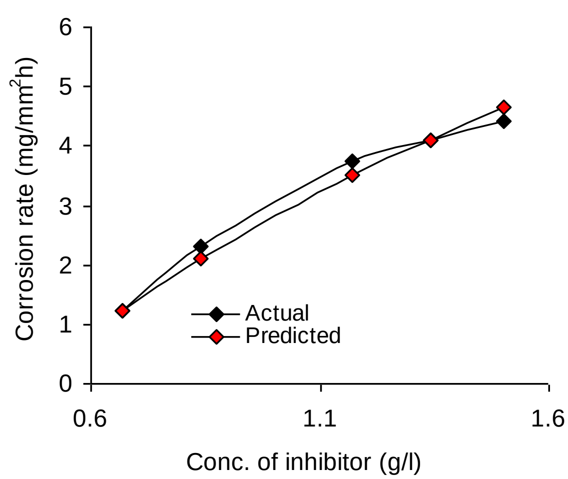

Fig. 4: Variation of corrosion rates with concentration of inhibitor as obtained from actual and model-predicted results.

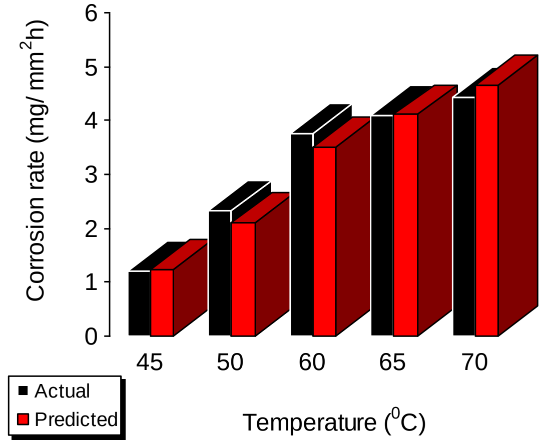

Fig. 5: Variation of corrosion rates with reaction temperature as obtained from actual and model- predicted results.

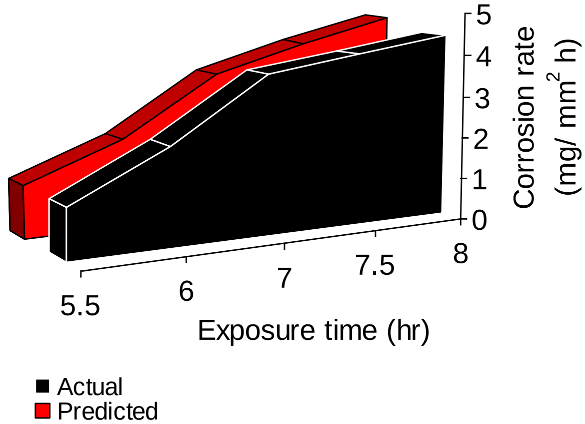

Fig. 6: Variation of corrosion rates with exposure time as obtained from actual and model-predicted results.

3.2.3 Deviational Analysis

Comparative analysis of the corrosion rate obtained from the actual and model-predicted results shows deviation on the part of model-predicted results. This was attributed to the fact that the effects of the surface properties of the mild steel which played vital roles during corrosion in H_2SO_4- chicken nail extract solution were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted corrosion rate to those of the corresponding experimental values.

The deviation Dv, of model-predicted corrosion rate from the corresponding actual result was given by

$$Dv = \left(\frac{ђ_P - ђ_E}{ђ_E}\right) \text{x } 100 \qquad (4)$$

Where

$ђ_E$ and $ђ_P$ are corrosion rates evaluated from experiment and derived model respectively

Fig.7 shows that maximum deviation of model-predicted corrosion rate from the actual results was less than 9.85%. This translates into over 90.15% model operational confidence. The figure shows that the least and highest deviations of model-predicted results (from actual results) are -0.53 and -9.83 %.

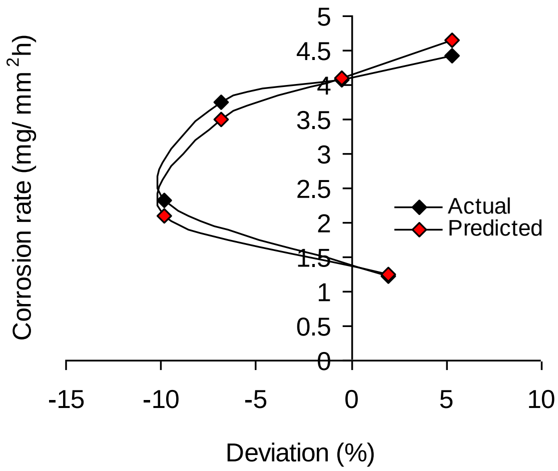

Fig. 7: Deviation of model–predicted results from actual values.

These deviations correspond to model-predicted corrosion rates: 4.1076 and 2.0929 (mg/mm^{2}h); reaction temperatures: 65 and 50 (^{0}C); exposure times: 7.5 and 6 (hrs) and inhibitor concentrations: 1.34 and 0.84 (g/l) respectively.

Correction factor, Cf to the model-predicted results was given by

$$Cf = - \left(\frac{\text{ђ}_P - \text{ђ}_E}{\text{ђ}_E} \times 100 \right) \qquad (5)$$

Comparative analysis of Fig. 7 and Table 3 shows that the evaluated correction factors are negative of the deviation as shown in equations (4) and (5).

Table 3: Variation of correction factor to model- predicted corrosion rate with the reaction temperature

Temp (^{0}C)	Cf (%)
45	- 1.93
50	+ 9.83
60	+ 6.89
65	+ 0.53
70	- 5.28

The correction factor took care of the negligence of operational contributions of the effects of surface properties of the mild steel which actually affected the corrosion process. Introduction of the corresponding values of Cf from equation (5) into the model gives exactly the corresponding actual corrosion rate.

Table 3 indicates that the maximum correction factor to the model-predicted corrosion rate was less than 9.85%. The table shows that the least and highest correction factors to the model-predicted results (from actual results) are 0.53 and 9.83%. These correction factors also correspond to model-predicted corrosion rates: 4.1076 and 2.0929 (mg/mm^{2}h); reaction temperatures: 65 and 50 (^{0}C); exposure times: 7.5 and 6 (hrs) and inhibitor concentrations: 1.34 and 0.84 (g/l) respectively. The deviation of model predicted results from that of the actual is just the magnitude of the value. The associated sign preceding the value signifies deviation deficit (negative sign) or surplus (positive sign).

4.0 Conclusion

Predictive analysis of mild steel corrosion rate during the inhibitive activities of Chicken nail extract in 2M sulphuric acid were carried out. The derived model shows that mild steel corrosion rate was a direct function of the sum of the natural logarithms of reaction temperatures, inhibitor concentrations and exposure times. An empirical model; $\text{ђ} = 1.3567 \ln \vartheta + 2.6196 \ln \beta + 3.1095 \ln \varepsilon – 13.49$ predicts the corrosion rate with maximum deviation < 9.85% (from actual results). This translated into over 91.15%operational confidence levels for the derived model. The validity of the model was rooted on the core model expression ђ

+ K = N ln ϑ + S lnβ + S_e lnε where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based corrosion rate relative to values of the actual results is 0.2258. The correlation coefficients between corrosion rate and reaction temperature, inhibitor concentration and exposure time were all > 0.97.

The derived model will predict the mild steel corrosion rate within the actual range, on substituting into the model, values of the inhibitor concentration, exposure time and reaction temperature, providing the boundary conditions are considered.

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