European Journal of Applied Sciences 12 (1): 19-24, 2020
ISSN 2079-2077

DOI: 10.5829/idosi.ejas.2020.19.24

Factorial Analysis of Mild Steel Corrosion Rate Based on Reaction Temperature and Inhibition Efficiency of Bilberry Cactus Extract in 1.5 M Hydrochloric Acid

[1]*C.I. Nwoye*, [2]*P.C. Nwosu*, [3]*I.E. Mbuka-Nwosu*, [2]*S.O. Ikegbula* and [2]*O.E.Obi*

[1]Chemical Systems and Data Research Laboratory Department of Metallurgical and Materials Engineering, Nnamdi Azikiwe University, Awka, Nigeria
[2]Department of Mechanical Engineering, Federal Polytechnic Nekede, Owerri, Nigeria
[3]Department of Environmental Engineering, Federal University of Technology, Owerri, Nigeria

Abstract: This paper presents the factorial analysis of mild steel corrosion rate based on the reaction temperature and inhibition efficiency of bilberry cactus extract in 1.5M hydrochloric acid. The analysis was carried out during the corrosion process within range of process parameters; 0.0036- 0.0056 (g cm^{-2} h^{-1}), 60.68- 70.83 (%) and 25- 35 (°C) for corrosion rate, inhibition efficiency and reaction temperature respectively. An empirical model; $\xi = 0.01\vartheta \text{ẞ}^{-1}$ derived for the evaluation process indicates that the mild steel corrosion is directly and inversely proportional to the reaction temperature and inhibition efficiency respectively; in agreement with experimental results. The validity of the model was rooted on the core model expression $\xi\, \text{ẞ} = \text{ƅ}\, \vartheta$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based corrosion rate relative to the actual results is 4.67E-05%. Further evaluations show that corrosion rates per unit rise in reaction temperature during the corrosion process were 0.00015 and 0.00021 (g cm^{-2} h^{-1})/°C as obtained from actual and model-predicted results respectively. This indicates significant proximity in the outputs. The maximum deviation of model-predicted results from those of the actual was < 10%. This translated into over 90% operational confidence level for the derived model. The correlation coefficients between corrosion rate and reaction temperature & inhibition efficiency were all > 0.99.

Key words: Analysis - Mild steel corrosion - Bilberry cactus extract - Hydrochloric acid

INTRODUCTION

Hydrochloric acid solutions are generally used in processes which are normally accompanied by considerable dissolution of the metal, drilling operations in oil and gas exploration, for cleaning, descaling, and pickling of steel structures. In order to protect metals and alloys deployed in service in HCl infested environments against corrosion, some species are added to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate [1-3].

Based on the foregoing, the application of organic compounds containing nitrogen, oxygen, or sulfur as inhibitors to metals in HCl acid solution has received considerable applause due its readiness to retard corrosion attack [4-8]. These inhibitors normally act at the interface created by corrosion products between the steel and aqueous corrosive solution. The researchers [9] reported that their interaction with the corroding mild steel surface through adsorption, results in a modification in the rate of the corrosion process. Furthermore, the adsorption strengths of these organic inhibitors were determined by structural, mechanical, and chemical characteristics of the adsorption layers formed under specific conditions.

Results of investigation [10] on the inhibiting effect of aqueous extracts of Funtumia elastica (FE) on mild steel corrosion in 1M HCl solution using electrochemical and surface characterization techniques revealed that FE effectively inhibited the corrosion reaction. Polarization data reveal that the extract functioned as a mixed-type inhibitor, while impedance results show that the extract organic matter gets adsorbed on the metal/solution interface. Atomic force microscopy, Fourier transform infrared spectroscopy

Corresponding Author: C.I. Nwoye, Chemical Systems and Data Research Laboratory, Department of Metallurgical and Materials Engineering, NnamdiAzikiwe University, Awka, Nigeria.
E-mail: nwoyennike@gmail.com

and scanning electron microscopy results confirmed the formation of a protective layer of extract adsorbed on the mild steel surface. Quantum chemical computations and molecular dynamics simulations, in the framework of the density functional theory was used for theoretical description of adsorption of some organic constituents of FE on mild steel.

Studies [11, 12] has shown that the basic components of extracts are sugars, gallic acid, ellagic acid and flavanoids. The presence of tannins, cellulose and polycyclic compounds normally enhances the film formation over the metal surface, thus decreasing corrosion [13, 14]. Scientists [15-25] have appraised and reported the possibility of using these highlighted natural products such as extracted compounds from leaves or seeds as corrosion inhibitors.

Investigation [26] has be carried out on the inhibition efficiency of Chrysophyllum albidum extract in controlling corrosion of mild steel in 1 M HCl using weight loss, potentio dynamic polarization and electrochemical impedance techniques at 303 K. The study also considered the effect of immersion time and temperature on inhibition efficiency of the extract was also studied. Results of the investigation indicate that inhibition increased with increasing concentration of the extract but decrease with increasing time and temperature. Data from electrochemical measurements suggest that the extract functioned by adsorption of the organic matter on the metal/corrodent interface, inhibiting both the anodic and cathodic half reactions of the corrosion process. The increase in concentration of the inhibitor causes an increase in the activation energy and a decrease in the exponential factor k.

It was also observed that the plant extracts follow Langmuir adsorption isotherm. Moreover, the process of adsorption was spontaneous, stable and considered to be physical adsorption. The thermodynamic properties recorded suggest that the process of film formation is higher than the destruction of the metal surface and that the adsorption process is exothermic.

It has been observed [27] that the protective film formed on the surface of the mild steel during inhibition of bilberry cactus extract on mild steel in 1.5 M HCl was as a result of adsorption of the extracts which obeyed Langmuir adsorption is otherm. The investigation was carried out at a temperature and extract concentration range of 30-60°C and 0.1 -0.5 g/l respectively using weight loss and hydrogen evolution measurement method.

An empirical model; ξ = V(ϑ/ჵ)$^{0.0001}$ was derived [28] to evaluate the corrosion inhibition efficiency (due to weight loss) of bilberry cactus extract on the mild steel. The validity of the model was rooted on the core model expression (ჵ/ϑ)$^{0.0001}$ = V/ξ where both sides of the expression are correspondingly equal to unity. The standard error incurred in predicting the model-based inhibition efficiencies (due to weight loss) relative to the actual results is 0.8668. Deviational analysis of model-predicted results with respect to actual results was < 3%. This translated into over 97% operational confidence levels for the derived model. The correlation coefficients between inhibition efficiency (due to weight loss) and corrosion rate, hydrogen evolution rate &inhibition efficiency (due to hydrogen evolution) were all > 0.97.

The aim of this research is to take a factorial analysis of the mild steel corrosion rate based on the reaction temperature and inhibition efficiency of Bilberry cactus extract in hydrochloric acid solution.

MATERIALS AND METHODS

Materials used for the experiments are mild steel coupons (of composition; carbon 0.053%, silicon 0.14%, aluminium 0.2%, calcium 0.1%, manganese 0.48%,iron 97.48%, copper 0.057% and chromium 0.018%), 1.5M HCl solution (prepared by dilution of analytical grade 37% HCl with double distilled water), bilberry cactus plant, distilled water. The equipment used were pyrex beakers Micro drilling machine (Model H), analytical digital weighing machine (Mettle 4900) and pH meter. Other materials used and detailed experimental procedures are as shown in previous work [27].

RESULTS AND DISCUSSION

Table 1: Variation of mild steel corrosion rate ξ with inhibition efficiency ჵ of bilberry cactus extract and reaction temperature ϑ respectively [27]

(ϑ)	(ჵ)	(ξ)
25	70.83	0.0036
28	68.48	0.0040
30	66.92	0.0043
33	64.58	0.0048
35	63.02	0.0051

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

ξ ჵ =Ђϑ (1)

Introducing the value of Ђ into equation (1) reduces it to;

ξ =0.01 (ϑ / ჵ) (2)

The derived model is equation (2).

where

ƀ = 0.01; equalizing constant (determined using C-NIKBRAN [29])

(ϑ) = Reaction temperature (°C)

(ꝭ) = Inhibitor efficiency (%)

(ξ) = Corrosion rate (due to weight loss) (g cm^{-2} h^{-1})

Boundary and Initial Conditions: A short cylindrically shaped mild steel coupon was considered, submerged in hydrochloric acid-bilberry cactus extract solution, interacting with some corrosion-induced agents. The solution is assumed to be affected by undesirable dissolved gases. The considered range are 0.0036-0.0056 (g cm^{-2} h^{-1}), 63.02-70.83 (%) and 25- 35(°C) for corrosion rate, inhibition efficiency and reaction temperature respectively.

Table 2: Variation of ξ ꝭ with ƀϑ

ξ ꝭ	ƀϑ
0.2550	0.2500
0.2739	0.2800
0.2878	0.3000
0.3100	0.3300
0.3214	0.3500

Model Validity: Equation (2) is the derived model. The validity of the model is rooted on the core model equation (1) where both sides of the equation are correspondingly almost equal. Table 2 also agrees with equation (1) considering values of ξꝭ and ƀϑ computed from the actual results in Table 1. Furthermore, the derived model was validated by comparing the corrosion rate predicted by the model and that obtained from the experiment. This was done using various analytical techniques which includes computational, statistical, graphical and deviational analyses.

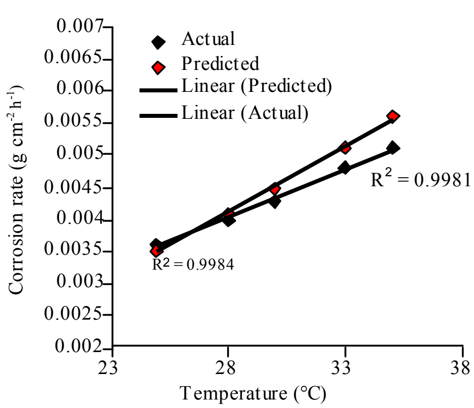

Fig. 1: Coefficient of determination between corrosion rate and reaction temperature as obtained from actual and model-predicted results

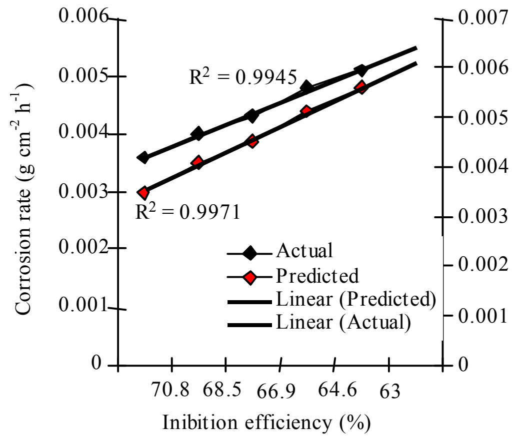

Fig. 2: Coefficient of determination between corrosion rate and inhibition efficiency as obtained from actual and model-predicted results

Computational Analysis

Corrosion Rate Per Unit Rise In Reaction Temperature: The corrosion rate per unit rise in reaction temperature ξ_ϑ (g cm^{-2} h^{-1})/°C was calculated from the equation;

$$\xi_\vartheta = \xi / \vartheta \quad (3)$$

Re-written as

$$\xi_\vartheta = \Delta \xi / \Delta\vartheta \quad (4)$$

Equation (4) is detailed as

$$\xi_\vartheta = \xi_2 - \xi_1 / \vartheta_2 - \vartheta_1 \quad (5)$$

where

ξ_ϑ = Change in the corrosion rates ξ_2, ξ_1 atreaction temperature values ϑ_2, ϑ_1.

Considering the points (25, 0.0036) & (35, 0.0051), (25,0.0035) &(35,0.0056) as shown in Fig. 1, designating them as (ϑ_1, ξ_1) &(ϑ_2, ξ_2) for actual and model-predicted results, and then substituting them into equation (5), gives the slopes: 0.00015, and 0.00021 (g cm^{-2} h^{-1})/°C respectively as their corresponding corrosion rates per unit rise in reaction temperature during the corrosion process.

Statistical Analysis

Correlation: The correlation coefficient between corrosion rate and reaction temperature & inhibition efficiency were evaluated (using Microsoft Excel Version 2003) from results of the actual and derived model. These results are

0.9990 and 0.9992 & 0.9972 and 0.9985 respectively. The evaluations were based on the coefficients of determination R^2 shown in Fig. 1, Fig. 2 and calculated using equation (6).

$$R=\sqrt{R^2} \quad (6)$$

Standard Error (STEYX): The standard error incurred in predicting the model-based corrosion rate relative to values of the actual results is 4.67E-05%. The standard error was evaluated using Microsoft Excel version 2003.

Graphical Analysis: Figs. 3 and 4 show curves and shapes perimeters of model-predicted and actual results with high degree of alignment. This invariably indicates proximate agreement between both results.

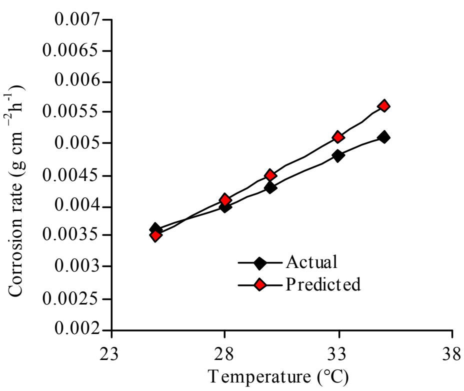

Fig. 3: Variation of corrosion rates with reaction temperature as obtained from actual and model-predicted results

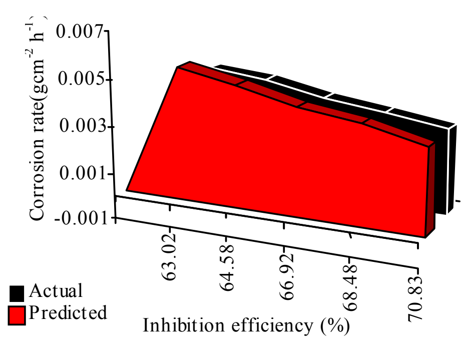

Fig. 4: Variation of corrosion rates with inhibition efficiency as obtained from actual and model-predicted results

Deviational Analysis: Comparative analysis of the mild steel corrosion rate obtained from the actual and model-predicted results shows single digit 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 hydrochloric acid- bilberry cactus 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

$$Dv = \left(\frac{\xi_P - \xi_E}{\xi_E}\right) x\ 100 \quad (7)$$

where,
ξ_E and ξ_P are corrosion rates evaluated from experiment and derived model respectively

Fig.5 shows that maximum deviation of model-predicted corrosion rate from the actual results was less than 10%. This translates into over 90% model operational confidence. The figure shows that the least and highest deviations of model-predicted results (from actual results) are – 1.94 and 9.8 %.

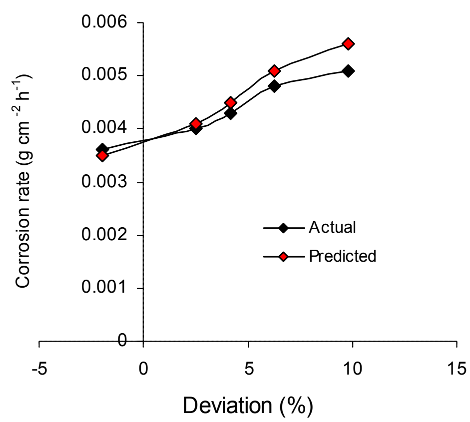

Fig. 5: Deviation of model–predicted results from actual values relative to corrosion rate

These deviations correspond to model-predicted corrosion rates: 0.00353 and 0.0056 (g cm^{-2} h^{-1}); reaction temperature: 25 and 35 (°C) and inhibition efficiency: 70.83 and 63.02 (%) respectively.

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

$$Cf = -\left(\frac{\xi_P - \xi_E}{\xi_E}\right) x\ 100 \quad (8)$$

Comparative analysis of Fig. 5 and Fig. 6 show that the evaluated correction factors are negative of the deviation as shown in equations (7) and (8).

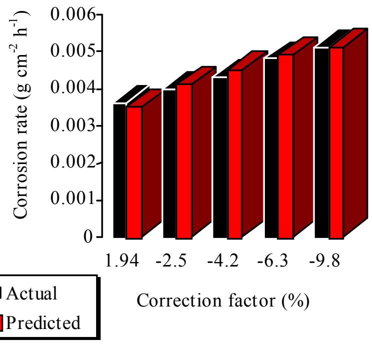

Fig. 6: Correction factor to model–predicted results relative of corrosion rate

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 (8) into the model gives exactly the corresponding actual corrosion rate. Fig. 6 indicates that the maximum correction factor to the model-predicted was less than 10%. Fig 6 shows that the least and highest correction factors to the model-predicted results are 1.94 and – 9.8 %. These deviations correspond to model-predicted corrosion rates: 0.00353 and 0.0056 (g cm^{-2} h^{-1}); reaction temperature: 25 and 35 (°C) and inhibition efficiency: 70.83 and 63.02 (%) 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).

CONCLUSION

Factorial analysis of mild steel corrosion rate was carried out based on the reaction temperature and inhibition efficiency of bilberry cactus extract in 1.5M hydrochloric acid. An empirical model; $\xi = 0.019\vartheta$ᶊ$^{-1}$ derived for the evaluation process indicates directly and inversely relationship between mild steel corrosion rate and reaction temperature & inhibition efficiency respectively; in agreement with experimental results. The validity of the model was rooted on the core model expression ξ ᶊ = ƅ ϑ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based corrosion rate relative to the actual results is 4.67E-05%. Further evaluations show that corrosion rates per unit rise in reaction temperature during the corrosion process were 0.00015 and 0.00021 (g cm^{-2} h^{-1})/ °C as obtained from actual and model-predicted results respectively. This indicates significant proximity in the outputs. The maximum deviation of model-predicted results from those of the actual was < 10%. This translated into over 90% operational confidence level for the derived model. The correlation coefficients between corrosion rate and reaction temperature & inhibition efficiency were all > 0.99.

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