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Response of mild steel corrosion rate in h_2so_4 solution to the input concentration of hypoxanthine as inhitor and its inhibition efficiency

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Abstract

This paper evaluates the response of mild steel corrosion rate to the inhibitor (hypoxanthine) concentration and inhibition efficiency using a derived empirical model; $\xi = ꝋ\gamma^{-K} + ђ\eta^{-N}$. In the course of the derivation, the range of values for the process parameters used were 2.46 x 10^{-4} - 2.98 x 10^{-4} (g $h^{-1}cm^{-2}$), 0.002-0.01(mol dm^{-3}) and 53.98- 61.94 (%) for corrosion rate, inhibitor concentrations and inhibition efficiencies respectively. The validity of the model is strongly rooted on the core model structure; $\xi - ђ\eta^{-N} \approx ꝋ\gamma^{-K}$. The model-predicted results agree with previous research on the inverse relationship between the corrosion rate and inhibitor concentration & inhibition efficiency. The standard error incurred in predicting the model based corrosion rates relative to the actual results was < 0.04%, implying over 99% model confidence level. Corrosion rate per unit inhibitor concentration and inhibition efficiency were evaluated as - 0.0065 & - 0.00625 g h^{-1} cm^{-2} /mol dm^{-3} and - 6.53 x 10^{-6} & - 6.28 x 10^{-6} g h^{-1} cm^{-2} / %, using the actual and model-predicted results respectively. Furthermore, the correlations between these highlighted parameters, as evaluated from both results were all > 0.96. The overall maximum deviation of model-predicted corrosion rate from actual results was 5.62%.

Keywords: Mild steel, corrosion rate, sulphuric acid, hypoxanthine, inhibition efficiency

1. Introduction

Catastrophic failures of structural facilities involving steel pipelines and vessels have been a recurring issue in the oil and gas industries. This set back gulps a large sum of money to put the structures on track, while the unforeseen resultant environmental degradation due to oil spillage, sets in destructive imbalance in the ecosystem. Complete hindrance of corrosion and any other forms of metal and alloy degradation due to oxidation is basically impossible. However, macromolecules can hinder or control the highlighted process to a reasonable extent (Nwanonenyi et al., 2016). Macromolecules are large molecules built up by repetition of smaller molecules (monomers). These smaller molecules are mostly polymeric in nature and covalently bonded together. Applicability of macromolecules includes usage as binders and thickeners in surface coating, dyes, pigments as a result of the ease with which their physical and chemical properties are processed and modified.

Some properties of polymer (synthetic and natural) have conferred on it global acceptability as inhibitor against corrosion of metals and alloys in various aggressive environments. These properties include low cost, renewability, non-toxicity, biodegradability, availability and water solubility. Furthermore, presence of multiple substituent and functional group either in their back bone or side chains are basic determining factors in the preferment of polymers and their blends over simple organic compounds as inhibitors for corrosion control. Extracts from natural plants (Obot et al., 2014; Nwanonenyi et al., 2016; Nwanonenyi et al., 2016) have also been used as corrosion inhibitors. Research by Nwoye et al., (2020) has shown that the corrosion current density $í_{corr}$ 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;

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

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, in line with previous work (Nwanonenyi et al., 2016). The decrease in the corrosion current density basically implies reduction in corrosion attack on the aluminum. The validity of the model was rooted on the core model expression $í_{corr}$ - K = - Ђη -Nϑ 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%.

Multi-factorial evaluation of the corrosion inhibition efficiency (due to weight loss) of bilberry cactus extract on mild steel in hydrochloric acid solution has been reported (Nwoye & Okelekwe, 2020). Reaction between the mild steel and HCl during the corrosion process resulted to hydrogen evolution. Hydrogen evolution rate was directly proportional to the mild steel corrosion rate. Furthermore, inhibition efficiencies due to weight loss and hydrogen evolution were evaluated to be directly proportional and almost equal. This implied that the mild steel corrosion was as a result of the hydrogen evolution. An empirical model;

ξ = Ѵ(ϑ /₰)^0.0001 (2)

was derived 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 (₰/ϑ)^0.0001 = Ѵ/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 was 0.8668. 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 maximum discrepancy between the model-predicted results and actual results was < 3%. This translated into over 97% operational confidence levels for the derived model.

Hypoxanthine has been successfully used (Momoh-Yahaya et al., 2014) as an impactful 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 with increase in the concentration and inhibition efficiency of the inhibitor. Thorough investigation revealed that no existing mathematical expression confirmed this relationship. This therefore raised the need for the present work to fill in the gap.

The present work aims at mathematically deriving the dependence of mild steel corrosion rate on the input concentration of hypoxanthine (inhibitor) and its inhibition efficiency. It is strongly believed that the model if derived will predict the corrosion rate of mild steel serving in sulphuric acid solution, within the range of experimental values, following substitution into the model, values of the inhibitor concentration and its inhibition efficiency, providing the boundary conditions are considered.

2.0 Material and methods

2.1 Methods

2.1.1 Gravimetric analysis; Weight loss measurements were carried out in accordance with an earlier report (Momoh-Yahaya et al., 2013). Tests were conducted under total immersion conditions in 150 mL of the aerated and unstirred test solutions. Immersion time varied from 1 to 5 days (120 h) in 0.1 M H_2SO_4. The coupons were retrieved from test solutions after every 24 h, appropriately cleaned, dried and reweighed. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight.

The corrosion rates of the alloy in the various environments were calculated using the relationship;

$$\xi = \frac{K\,\Delta W}{\rho A\, t} \qquad (3)$$

Where, A = Exposed area (mm^2), ρ = Density of the mild steel (g/cm^2), t = time (year), K = 87.5 (corrosion rate constant for mm/yr), Δw = Weight loss following corrosion (g)
The efficiency of the inhibitor used was evaluated using the expression;

$$\eta = \left(\frac{C_a - C_i}{C_a} \times 100\right) \qquad (4)$$

Where, C_a = Corrosion rate in absence of inhibitor (mm/yr), C_i = Corrosion rate in presence of inhibitor (mm/yr).

2.2 Model Derivation

Table 1: Variation of mild steel corrosion rate with inhibitor concentration and inhibition efficiency (Momoh-Yahaya et al., 2014).

(ξ)	(γ)	(η)
0.000298	0.002	53.98
0.000266	0.004	58.81
0.000264	0.006	59.23
0.000259	0.008	60.00
0.000246	0.01	61.94

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

$$\xi - \text{Ƀ}\eta^{-N} \approx \text{Ꝋ}\gamma^{-K} \qquad (5)$$

$$\xi = \text{Ꝋ}\gamma^{-K} + \text{Ƀ}\eta^{-N} \qquad (6)$$

The derived empirical model in the expression; (6) predicts the corrosion rate of mild steel in H_2SO_4 solution at known input concentration of hypoxanthine (inhibitor) and its operational inhibition efficiency. The model is a sum of two parts, consisting two power expressions. Table 1 and Table 2 show that ξ, γ and η are the mild steel corrosion rate (g h^{-1} cm^{-2}), inhibitor concentration (mol dm^{-3}) and inhibition efficiency (%) respectively. The equalizing constants; Ꝋ, K, Ƀ and N are 0.0001, 0.1066, 0.027 and 1.3721 respectively. They were generated using a software (Nwoye, 2008).

3.0 Results and Discussions

3.1 Boundary and Initial Conditions

Consider short cylindrically shaped mild steel coupon submerged in suphuric acid, interacting with some corrosion-induced agents. The solution is assumed to be affected by undesirable dissolved gases. The considered range of the corrosion rate, inhibitor concentrations and inhibition efficiencies are 2.46 x 10^{-4} - 2.98 x 10^{-4} (g $h^{-1}cm^{-2}$), 0.002-0.01(mol dm^{-3}) and 53.98- 61.94 (%) respectively.

Table 2: Variation of ξ – Ђη^{-N} with ·Ɵγ^{-K}

ξ – Ђη^{-N}	·Ɵγ^{-K}
0.000185	0.000194
0.000165	0.000180
0.000164	0.000173
0.000161	0.000167
0.000152	0.000163

3.2 Model Validity

Validity of the derived model is strongly rooted on the core model structure; ξ – Ђη^{-N} ≈ ·Ɵγ^{-K} expressed in equation (5), both sides of which are correspondingly approximately equal. Furthermore, Table 2 agrees with the model structure following results of evaluation of its various components, computed from experimental results in Table 1. Furthermore, the derived model was validated by carrying out deviational analysis, comparing the model-predicted results with experimental values, and also evaluating the correlations and standard errors.

3.2.1 Graphical Analysis

Graphical analysis of Fig. 1 and Fig. 2 show aligned curves of mild steel corrosion rate, relative to inhibitor input concentration and inhibition efficiency respectively. The curves in each figure, represent model-predicted and experimental results. These curves significantly show in each case similar spread & trend of data point distribution, and also corresponding point-to-point proximate values. The curves are negatively oriented, and would likely emphasize negative slopes. This follows the inverse relationship between mild steel corrosion rate and inhibitor concentration & inhibition efficiency.

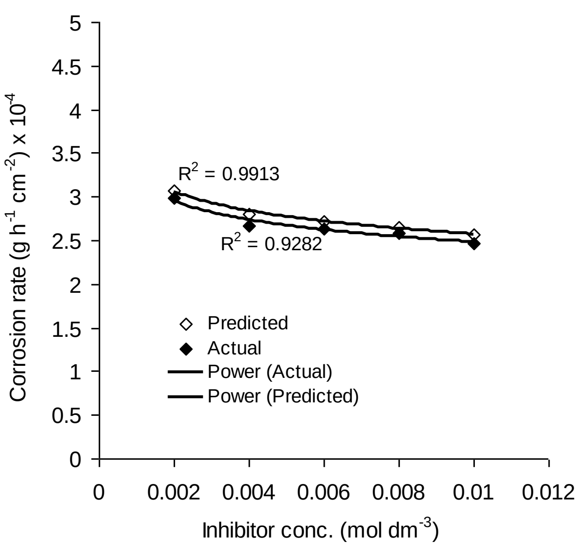

Fig.1: Comparison of mild steel corrosion rate (relative to inhibitor concentration) from actual and derived model

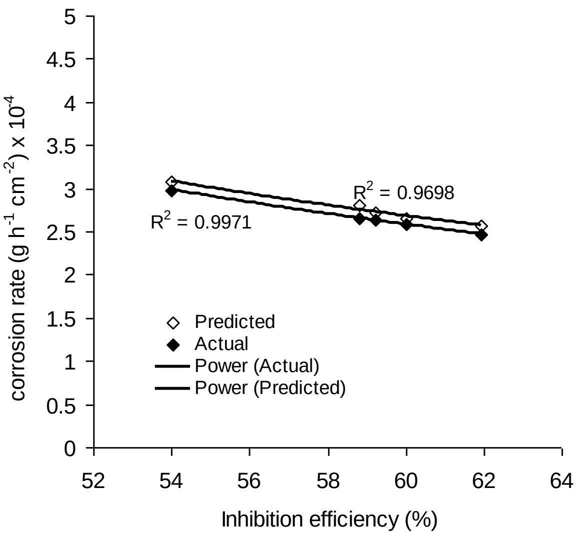

Fig.2: Comparison of mild steel corrosion rate (relative to inhibition efficiency) from actual and derived model

3.2.2 Statistical analysis

3.2.2.1 Correlation

The correlation coefficient between mild steel corrosion rate and inhibitor concentration & inhibition efficiency were evaluated (using Microsoft Excel Version 2003 from the coefficient of determinants on the actual and model-predicted results of Figs. 1 and 2, using equation (7).These results are 0.9634 and 0.9956 & 0.9985 and 0.9848 respectively.

$$R = \sqrt{R^2} \quad (7)$$

3.2.1.2 Standard Error (STEYX)

The standard error incurred associating model prediction of mild steel corrosion rate relative to values of the actual results is less than 0.04 %. This translates into over 99% model confidence level. The standard error was evaluated using Microsoft Excel version 2003.

3.2.3 Deviational Analysis

The functionality and acceptability of a derived model largely depends on the deviation of model-predicted result from corresponding experimental value. Fig. 3 shows Z–shaped curves, representing experimental and model-predicted mild steel corrosion rates, relative to the evaluated percent deviation by model-predicted values. Deviational analysis carried out on model-predicted results with respect to those of the experiment gave 5.62% as maximum. This gives over 94% model confidence level. It therefore holds that the operational range of the model confidence level places between 94- 99%, considering evaluations from standard error, correlations and maximum deviation. Fig. 3 shows that the least and highest deviations of model-predicted mild steel corrosion rate (from actual results) are 2.32 and 5.62 % respectively. These deviations correspond to model-predicted mild steel corrosion rates: 0.000265 & 0.000281 g h^{-1} cm^{-2}, inhibitor concentrations: 0.008 & 0.004 mol dm^{-3} and inhibition efficiencies: 60.0 and 58.81% respectively.

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

$$Dv = \left(\frac{\xi_m - \xi_E}{\xi_E} \times 100\right) \quad (8)$$

Where ξ_m and ξ_E are corrosion rates evaluated from actual and model-predicted results respectively

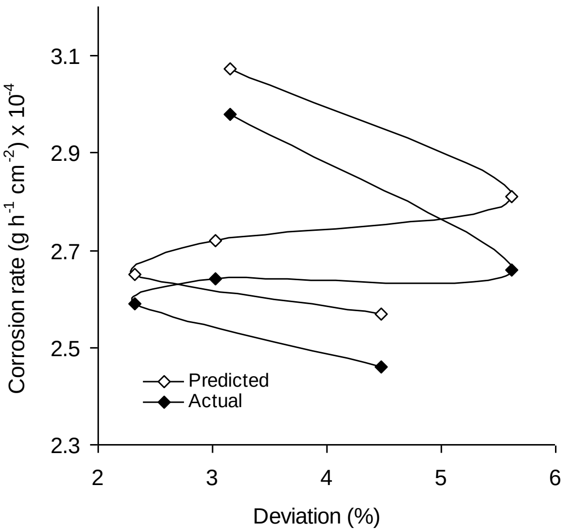

Fig. 3: Variation of model-predicted mild steel corrosion rate with its corresponding deviation from experimental results

It is instructive to conclude that model results deviation from corresponding experimental values prompted from, non-consideration during model formulation, the effects of surface properties of the mild steel and physicochemical interaction between the steel, acid and inhibitor, all of which play vital roles during the corrosion process. This necessitated the introduction of correction factor, to bring the model-predicted corrosion rates to those of the corresponding experimental values.

Corrosion rate per unit inhibitor input concentration ξ_γ (g h^{-1} cm^{-2} /mol dm^{-3}) was calculated from the equation;

$$\xi_\gamma = \xi / \gamma \quad (9)$$

The expression (9) is re-written as;

$$\xi_\gamma = \Delta\xi / \Delta\gamma \quad (10)$$

detailed as

$$\xi_\gamma = \xi_2 - \xi_1 / \gamma_2 - \gamma_1 \quad (11)$$

Where

$\Delta\xi$ = Change in the corrosion rates ($\xi_2 - \xi_1$) at two inhibitor concentrations γ_2, γ_1.

$\Delta\gamma$ = Change in the inhibitor concentrations γ_2, γ_1

A plot of points (0.002, 0.000298) and (0.01, 0.000246) for (γ_1, ξ_1) and (γ_2, ξ_2) respectively (as in Fig. 1) and substituted into the expression (11), gives a slope; - 0.0065 g h^{-1} cm^{-2} /mol dm^{-3} . This is the corrosion rate per unit inhibitor concentration during the actual corrosion process. Similarly a plot (as in Fig. 1) using model-predicted results gives a slope; - 0.00625 g h^{-1} cm^{-2} /mol dm^{-3} on substituting points (0.002, 0.000307) and (0.01, 0.000257) for (γ_1, ξ_1) and (γ_2, ξ_2) respectively into equation (11). A comparison of these two values shows proximate agreement.

Corrosion rate per unit inhibition efficiency ξ_η (g h^{-1} cm^{-2} / %) was calculated from the equation;

$$\xi_\eta = \xi / \eta \quad (12)$$

The equation (12) is re-written as;

$$\xi_\eta = \Delta\xi / \Delta\eta \quad (13)$$

detailed as

$$\xi_\eta = \xi_2 - \xi_1 / \eta_2 - \eta_1 \quad (14)$$

Where

$\Delta\xi$ = Change in the corrosion rates ($\xi_2 - \xi_1$) at two inhibition efficiencies η_2, η_1.

$\Delta\eta$ = Change in the inhibition efficiencies η_2, η_1

Plotting points (53.98, 0.000298) & (61.94, 0.000246) and (53.98, 0.000307) & (61.94, 0.000257) for (η_1, ξ_1) and (η_2, ξ_2) as shown in Fig. 2, and then substituting them into the equation (14), gives slopes; - 6.53 x 10^{-6} and - 6.28 x 10^{-6} g h^{-1} cm^{-2} / % as corrosion rate per unit inhibition efficiency evaluated from experimental and model-predicted results respectively. The negative signs preceding the evaluated slopes just indicate an inverse relationship between the corrosion rate and inhibitor concentration & inhibition efficiency. The real slopes are the modulus of the values.

4.0. Conclusion

The response of mild steel corrosion rate to the inhibitor (hypoxanthine) concentration and inhibition efficiency was evaluated using a derived empirical model; ξ = Ꞓγ^{-K} + Ꞑη^{-N} .The validity of the model is strongly rooted on the core model structure; ξ – Ꞑ$\eta^{-N} \approx$ Ꞓγ^{-K}. The model-predicted results agree with previous research on the inverse relationship between the corrosion rate and inhibitor concentration & inhibition efficiency. The standard error incurred in predicting the model based corrosion rates relative to the actual results was < 0.04%, implying over 99% model confidence level. Corrosion rate per unit inhibitor concentration and inhibition efficiency were evaluated as - 0.0065 & - 0.00625 g h^{-1} cm^{-2} /mol dm^{-3} and - 6.53 x 10^{-6} & - 6.28 x 10^{-6} g h^{-1} cm^{-2} / %, using the actual and model-predicted results respectively. The correlations between the corrosion rate and inhibitor concentration & inhibition efficiency, using actual and model-predicted results were all > 0.96. The overall maximum deviation of model-predicted corrosion rate from actual results was 5.62%. The derived model will predict the corrosion rate of mild steel in the acid solution, within the actual results range, on substituting into the model, values of the inhibitor concentration and inhibition efficiency, providing the boundary conditions are considered. The limitation of this work is that the mild steel corrosion rate cannot be predicted beyond the boundary conditions except through simulation.

References

Momoh-Yahaya H., Eddy N. O., Oguzie E. E. 2014. Inhibitive,Adsorption and Thermodynamic Study of Hypoxanthine against the Corrosion of Aluminium and Mild Steel in Sulphuric Acid. J. Materials Environment Sci. 5(1): 237 – 24

Momoh-Yahaya, H., Eddy, N.O., Iyun, J.F., Gimba, C.E., Oguzie, E. E. 2013. *J. Mater. Sci. Res.*, 2:59.

Nwanonenyi, S. C., Madufor, I. C., Nwuzor, I. C., Arinze, C. V.. 2016. Experimental and theoretical studies of inhibitive behaviour of millet starch on the corrosion of aluminium in sulphuric acid environment, International Journal of Engineering and Technologies. 8:1-13.

Nwanonenyi, S. C., Madufor, I. C., Uzoma, P., Nwuzor, I. C., 2016. Corrosion inhibition of mild steel in sulphuric acid environment using millet starch and potassium iodide, International Research Journal of Pure and Applied Chemistry. 12(2):1-15.

Nwanonenyi, S. C., Ogbobe, O., Madufor, I. C., Oguzie, E. E., 2016. Inhibitive performance of hydroxypropyl cellulose and potassium iodide on the corrosion of mild steel in sulphuric acid environment, American Chemical Science Journal.16:1-12.

Nwoye C. I. and Okelekwe N. M. 2020. Multi-factorial Evaluation of Corrosion Inhibition Efficiency of Bilberry Cactus Extract on Mild Steel in HCl acid Solution.World Journal of Chemistry. 15(1):9-14

Nwoye C.I., Amanze, K. O. Okelekwe N. M., Joseph M. and Ibe C. O. 2020. Response of Current Density to the Concentration and Inhibition Efficiency of Hydroxypropyl Cellulose on Aluminium in HCl Acid. World Journal of Chemistry. 15(2):30-36.

Nwoye, C. I. 2008. Data Analytical Memory; C-NIKBRAN

Obot, I. B., Gasem, Z. M., Umoren, S. A. 2014. Molecular level understanding of the mechanism of aloes leaves extract inhibition of low Carbon steel corrosion: A DFT Approach, Int. J. Electrochem. Sci. 9:510-522