

Response of Hydrogen Evolution Rate to the Reaction Temperature and Corrosion Rate of Mild Steel Inhibited by Bilberry Cactus Extract in Hydrochloric Acid Solution

¹O.K. Orieko, ²P.C. Nwosu, ²D.C. Ugwuegbu, ²K.D. Ogukunle, ²S.O. Ikegbula and ²O.E. Obi

¹Department of Mechanical Engineering, Federal University of Technology, Owerri, Nigeria

²Department of Mechanical Engineering, Federal Polytechnic Nekede, Owerri, Nigeria

Abstract: The response of hydrogen evolution rate to the reaction temperature and corrosion rate of mild steel inhibited by bilberry cactus extract in hydrochloric acid was evaluated. The range of values process parameters considered were 0.0043- 0.0086 ($\text{g cm}^{-2} \text{h}^{-1}$), 0.016- 0.0568 ($\text{ml cm}^{-2} \text{min}^{-1}$) and 30- 60 ($^{\circ}\text{C}$) for corrosion rate, hydrogen evolution rate and reaction temperature respectively. A model; $V = k(\text{Log } \theta)^b$ was derived to evaluate the hydrogen evolution rate as a function of corrosion rate and powered logarithm of reaction temperature. The model shows mathematically that hydrogen evolution rate is affected by the reaction temperature and corrosion process, the later progressing with drop in hydrogen ion concentration. The validity of the model was rooted on the core model expression $(k/V) = ((\text{Log } \theta)^b)^{-1}$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based hydrogen evolution rate relative to the actual results is 1.830%. Further evaluations show that hydrogen evolution rates per unit rise in reaction temperature during the corrosion process were 0.00136 and 0.00145 ($\text{ml cm}^{-2} \text{min}^{-1}/^{\circ}\text{C}$) as obtained from actual and model-predicted results respectively. This indicates significant proximity in the outputs. Deviation analysis of model-predicted results with respect to actual results was $< 6.1\%$. This translated into over 93.9% operational confidence levels for the derived model. The correlation coefficients between hydrogen evolution rate and reaction temperature & corrosion rate were all > 0.97 .

Key words: Response - 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: P.C. Nwosu, Department of Mechanical Engineering, Federal Polytechnic, Nekede, Owerri, Nigeria.
E-mail: piusnwosu@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 been carried out on the inhibition efficiency of *Chrysophyllum albidum* extract in controlling corrosion of mild steel in 1 M HCl using weight loss, potentiodynamic 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/corrosion 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 isotherm. 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.

The aim of this research is to evaluate the response of hydrogen evolution rate to the reaction temperature and corrosion rate of mild steel inhibited by 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 (Mettler 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 hydrogen evolution rate V with mild steel corrosion rate \mathcal{K} and reaction temperature \mathcal{Q} respectively [27]

(\mathcal{Q})	(\mathcal{K})	(V)	($\text{Log } \mathcal{Q}$) ^b
30	0.0043	0.0160	3.7024
35	0.0047	0.0212	4.2964
40	0.0051	0.0264	4.8627
45	0.0055	0.0311	5.4031
50	0.0059	0.0358	5.9219
55	0.0073	0.0463	6.4197
60	0.0086	0.0568	6.9002

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

$$\frac{1}{(\text{Log } \mathcal{Q})^b} = \left(\frac{\mathcal{K}}{V} \right) \quad (1)$$

Introducing the value of \mathcal{H} into equation (1) reduces it to;

$$V = \mathcal{K} (\text{Log } \mathcal{Q})^b \quad (2)$$

The derived model is equation (2).

where,

$\mathcal{H} = 3.3557$; equalizing constant (determined using C-NIKBRAN [11])

(\mathcal{Q}) = Reaction temperature (°C)

(\mathcal{K}) = Corrosion rate of mild steel ($\text{gcm}^{-2} \text{h}^{-1}$)

(V) = Hydrogen evolution rate ($\text{ml cm}^{-2} \text{min}^{-1}$)

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 of the initial solution temperatures, corrosion rate and hydrogen evolution rate are 30-60 (°C), 0.0043-0.0086 (g cm⁻² h⁻¹) and 0.016-0.0568 (ml cm⁻² min⁻¹) respectively.

Table 2: Variation of (ξ/V) with $1/(\text{Log } \theta)^b$

ξ/V	$1/(\text{Log } \theta)^{3.3557}$
0.2688	0.2701
0.2217	0.2328
0.1932	0.2056
0.1768	0.1851
0.1648	0.1689
0.1577	0.1558
0.1514	0.1449

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 (ξ/V) with $((\text{Log } \theta)^b)^{-1}$ evaluated 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.

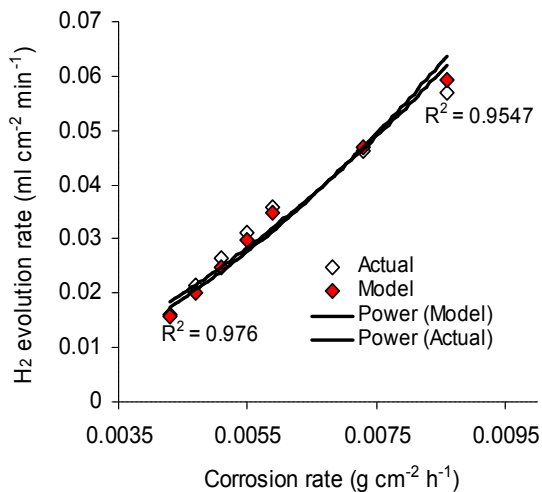


Fig. 1: Coefficient of determination between H₂ evolution rate and corrosion rate as obtained from actual and model-predicted results

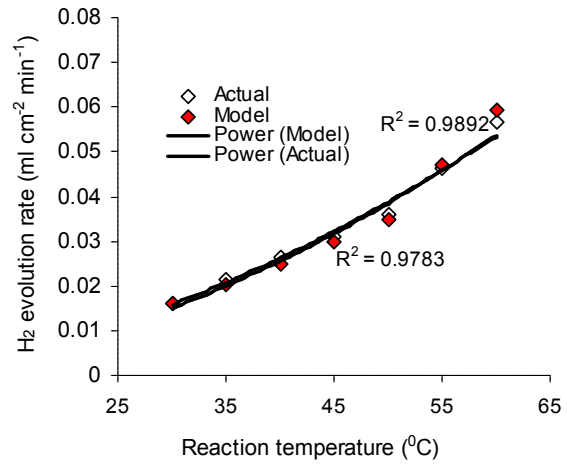


Fig. 2: Coefficient of determination between H₂ evolution rate and reaction temperature as obtained from actual and model-predicted results

Computational Analysis:

Hydrogen evolution rate per unit rise in reaction temperature

The hydrogen evolution rate per unit rise in reaction temperature V_{θ} (ml cm⁻² min⁻¹)/°C was calculated from the equation;

$$V_{\theta} = V / \theta \tag{3}$$

Re-written as

$$V_{\theta} = \Delta V / \Delta \theta \tag{4}$$

Equation (4) is detailed as

$$V_{\theta} = V_2 - V_1 / \theta_2 - \theta_1 \tag{5}$$

where

V_{θ} = Change in the hydrogen evolution rates V_2, V_1 at reaction temperature values θ_2, θ_1 .

Considering the points (30, 0.016) & (60, 0.0568), (30, 0.0159) & (60, 0.0593) as shown in Fig. 2, designating them as (θ_1, V_1) & (θ_2, V_2) for actual and model-predicted results, and then substituting them into equation (5), gives the slopes: 0.00136, and 0.00145 (ml cm⁻² min⁻¹)/°C respectively as their corresponding hydrogen evolution rates per unit rise in reaction temperature during the corrosion process.

Statistical Analysis

Correlation: The correlation coefficient between hydrogen evolution rate and reaction temperature & corrosion rate were evaluated (using Microsoft Excel Version 2003) from results of the actual and derived model. These results are 0.9946 and 0.9891 & 0.9771 and 0.9879 respectively. The evaluations were based on the coefficients of determination R^2 shown in Figs. 1-3 and calculated using equation (6).

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

Standard Error (STEYX): The standard error incurred in predicting the model-based hydrogen evolution rate relative to values of the actual results is 1.83%. 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

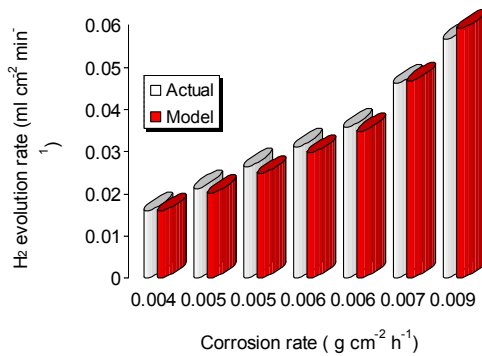


Fig. 3: Variation of H₂ evolution rate with corrosion rate as obtained from actual and model-predicted results

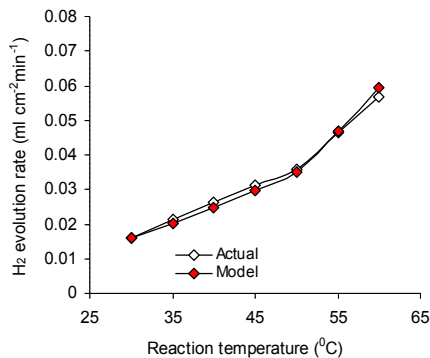


Fig. 4: Variation of H₂ evolution rate with reaction temperature as obtained from actual and model-predicted results

Deviational Analysis: Comparative analysis of the initial temperature of bilberry cactus extract-HCl solution precisely 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 initial solution temperature to those of the corresponding experimental values.

The deviation D_v , of model-predicted initial solution temperature from the corresponding actual result was given by

$$D_v = \left(\frac{\vartheta_p - \vartheta_E}{\vartheta_E} \right) \times 100 \quad (7)$$

where

ϑ_E and ϑ_p are initial solution temperatures evaluated from experiment and derived model respectively

Fig. 5 shows that maximum deviation of model-predicted reaction temperature from the actual results was less than 6.1%. This translates into over 93.9% model operational confidence. The figure shows that the least and highest deviations of model-predicted results (from actual results) are 0.63 and 6.06 %.

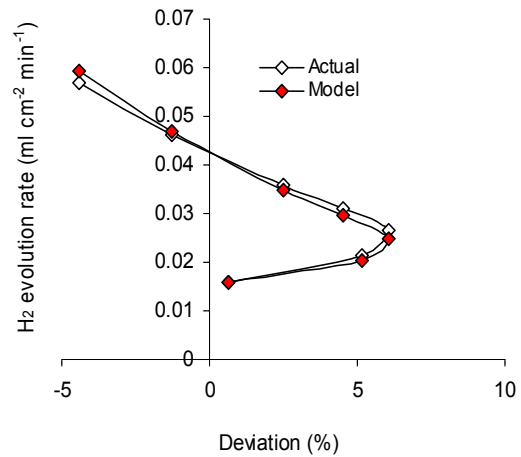


Fig. 5: Deviation of model-predicted results from actual values relative to H₂ evolution rate

These deviations correspond to model-predicted hydrogen evolution rates: 0.0159 and 0.0248 (ml cm⁻² min⁻¹); corrosion rates: 0.0043 and 0.0051 g cm⁻² h⁻¹ and reaction temperatures: 30 and 40 (°C) respectively.

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

$$Cf = - \left(\frac{\vartheta_P - \vartheta_E}{\vartheta_E} \right) \times 100 \quad (8)$$

Comparative analysis of Fig. 5 and Table 3 shows that the evaluated correction factors are negative of the deviation as shown in equations (7) and (8).

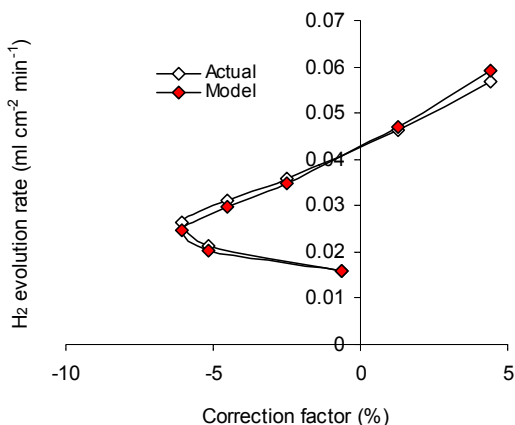


Fig. 6: Correction factor to model-predicted results relative to H₂ evolution rate

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 solution temperature. Fig. 6 indicates that the maximum correction factor to the model-predicted was less than 6.1%. Fig 6 shows that the least and highest correction factors to the model-predicted results are - 0.63 and - 6.06 %. These deviations correspond to model-predicted hydrogen evolution rates: 0.0159 and 0.0248 (ml cm⁻² min⁻¹); corrosion rates: 0.0043 and 0.0051 g cm⁻² h⁻¹ and reaction temperatures: 30 and 40 (°C) 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

The response of hydrogen evolution rate to the reaction temperature and corrosion rate of mild steel inhibited by bilberry cactus extract in hydrochloric acid was evaluated. A derived model; $V = \lambda (\text{Log } \vartheta)^b$ evaluated the hydrogen evolution rate as a function of

corrosion rate and powered logarithm of reaction temperature. The model showed mathematically that hydrogen evolution rate is affected by the reaction temperature and corrosion process, the later progressing with drop in hydrogen ion concentration. The validity of the model was rooted on the core model expression $(\lambda/V) = ((\text{Log } \vartheta)^b)^{-1}$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based hydrogen evolution rate relative to the actual results is 1.830%. Further evaluations show that hydrogen evolution rates per unit rise in reaction temperature during the corrosion process were 0.00136 and 0.00145 (ml cm⁻² min⁻¹)/°C as obtained from actual and model-predicted results respectively. This indicates significant proximity in the output. Deviation analysis of model-predicted results with respect to actual results was < 6.1%. This translated into over 93.9% operational confidence levels for the derived model. The correlation coefficients between hydrogen evolution rate and reaction temperature & corrosion rate were all >0.97.

REFERENCES

1. Zhang, S.T., Z.H. Tao, W.H. Li and B.R. Hou, 2009. The effect of some triazole derivatives as inhibitors for the corrosion of mild steel in 1M hydrochloric acid. *Appl. Surf. Sci.*, 255: 6757-6763.
2. Mohsen, L., R.A. Mohammad and M. Somaieh, 2010. The enhancing power of iodide on corrosion prevention of mild steel in the presence of a synthetic-soluble Schiff-base: *Electrochimica and surface analysis. Electrochim. Acta.*, 55: 6058-6063.
3. Chidiebere, M.A., E.E. Oguzie, L. Liu, Y. Li and F. Wang, 2014. Corrosion inhibition of Q235 mild steel in 0.5 M H₂SO₄ solution by phytic acid and synergistic iodide additives, *Ind. Eng. Chem. Res.*, 53: 7670-7679.
4. Shen, C.B., S.G. Wang, H.Y. Yang, K. Long and F.H. Wang, 2006. The adsorption stability and inhibition by ally-thiourea of bulk nano crystalline ingot iron in dilute HCl solution. *Appl. Surf. Sci.*, 253: 2118-2122.
5. Moretti, G.,F. Guidi and G. Grion, 2004. Trptamine as green iron corrosion inhibitor in 0.5 deaerated sulphuric acid. *Corros. Sci.*, 46: 387-403.
6. Quraishi, M.A. and D. Jamal, 2000. Dianils: New and Effective corrosion inhibition for oil-well steel (N80) and mild steel in boiling hydrochloric acid. *Corrosion*, 56(2): 156-160.

7. Khaled, K.F. and N. Hackerman, 2003. Investigation of the inhibitive effect of ortho-substituted anilines on corrosion of iron in 1 M HCl solutions. *Electrochim. Acta*, 48: 2715-2723.
8. Ali, Sk.A., M.T. Saeed and S.U. Rahman, 2003. The isoxazolidines: a new class of corrosion inhibitors of mild steel in acidic medium. *Corros. Sci.*, 45: 253-266.
9. Oguzie, E.E., C.B. Adindu, C.K. Enenebeaku, C.E. Ogukwe, M.A. Chidiebere and K.L. Oguzie, 2012. *J. Phys. Chem. C*, 116: 13603-13615.
10. Maduabuchi, A.C., Emeka, E. Oguzie, Li Liu, Ying Li and Fuhui Wang. 2015. Inhibitory Action of *Funtumia elastica* Extracts on the Corrosion of Q235 Mild Steel in Hydrochloric Acid Medium: Experimental and Theoretical Studies, *Journal of Dispersion Science and Technology*, 36:8.
11. Chen, G., M. Zhang, J. Zhao, R. Zhou, Z. Meng and Z. Zhang, 2013. Investigation of Ginkgo biloba leaf extracts as corrosion and oil field microorganism inhibitors. *Chem Cent J*, 7(83):1-7.
12. Gerengi, H., S.H. Katarzyna and I. Sahin, 2012. Corrosion inhibiting effect of Mimosa extracts on brass-MM55 corrosion in 0.5 M H₂SO₄ acidic media. *J. Ind. Eng. Chem.*, 18:2204-2210.
13. Sorkhabi, H.A. and E. Asghari, 2008. Effect of hydrodynamic conditions on the inhibition performance of L-methionine as a "green" inhibitor. *Electrochim Acta*, 54:162.
14. Martinez, S. and I. Stajlar, 2003. Correlation between the molecular structure and the corrosion inhibition efficiency of chestnut tannin in acidic solutions. *J. Mol Struct (Theochem)*, 640:167-174.
15. Oguzie, E.E., 2006. Studies on the inhibitive effect of *Occimum viridis* extract on the acid corrosion of mild steel. *Mater Chem. Phys.*, 99:441.
16. Okafor, A.P.C., M.E. Ikpi, I.E. Uwah, E.E. Ebenso, U.J. Ekpe and S.A. Umoren, 2008. Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media. *Corros Sci.*, 50:2310.
17. Radojicic, K., S. Berkovic and J.V. Kovac, 2008. Natural honey and black radish juice as tin corrosion inhibitors. *Corros Sci.*, 50:1498.
18. Ismail, K.M., 2007. Evaluation of cysteine as environmentally friendly corrosion inhibitor for copper in neutral and acidic chloride solutions. *Electrochim Acta*, 52:7811.
19. Chauhan, L.R. and G. Gunasekaran, 2007. Corrosion inhibition of mild steel by plant extract in dilute HCl medium. *Corros Sci.*, 49: 1143.
20. Gunasekaran, G. and L.R. Chauhan, 2004. Eco friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium. *Electrochim Acta*, 49:4387.
21. El-Etre, A.Y., 1998. Natural honey as corrosion inhibitor for metals and alloys in neutral aqueous solution. *Corros. Sci.*, 40:1845.
22. El-Etre, A.Y., 2003. Inhibition of aluminum corrosion using *Opuntia* extract. *Corros Sci.*, 45:2485.
23. El-Etre, A.Y., M. Abdallah and Z.E. El-Tantawy, 2005. Corrosion inhibition of some metals using lawsonia extract. *Corros. Sci.*, 47:385.
24. El-Etre, A.Y., 2006. Khillah, extract as inhibitor for acid corrosion of SX 316 steel. *Appl. Surf Sci.*, 252:8521.
25. Oguzie, E.E., 2008. Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel. *Corros. Sci.*, 50:2993.
26. Akalezi, C.O. and E.E. Oguzie, 2016. Evaluation of anticorrosion properties of *Chrysophyllum albidum* leaves extract for mild steel protection in acidic media. *International Journal of Industrial Chemistry*, 7:81-92.
27. Abdulrahman, A.S., I.H. Kobe, V.S. Aigbodion, K.A. Ganiyu and I.C. Awe, 2014. Thermodynamic behavior of mild steel corrosion in an environment of *Bilberry cactus* plant extracts in hydrochloric acid solution. *Journal Metallurgical and Materials Engineering*, 9: 1-14.
28. Nwoye, C.I., 2008. Data Analytical Memory; C-NIKBRAN.