

Computational Analysis of the Inhibition Efficiency of White Starch on Mild Steel Corrosion in 0.5M H₂SO₄ Based on Current Density and Inhibitor Concentration

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Abstract: This paper presents a computational analysis of the inhibition efficiency of white starch on mild steel corrosion in 0.5 M H₂SO₄ based on current density and inhibitor concentration. The analysis was carried out within a range of process parameter; 57.24-124.23 (μA cm⁻²), 0.2-0.8 (g/l) and 84.24-92.15 (%) for current densities, inhibitor concentrations and inhibition efficiencies are respectively. A derived empirical model; $\eta = 2.6 \ln i - 5.1 \ln i_{\text{corr}} + 113.1$ computes the corrosion inhibition efficiency of the white starch as subtraction of two natural logarithmic parts involving inhibitor concentration and current density. Results predicted by the model show that inhibition efficiency increases with increase in inhibitor concentration and decrease in the current density, in line with previous work. The decrease in the corrosion current density is an indication of reduction in corrosion attack on the mild steel. The validity of the model was rooted on the core model expression $\eta - K = \ln i - \ln i_{\text{corr}}$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based inhibition efficiency relative to the actual results was 0.29%. Evaluations from generated results indicate that the inhibition efficiency per unit inhibitor concentration as obtained from the actual and model-predicted results are 13.05 and 12.60%/(g/L) respectively. Maximum deviation of model-predicted results (from actual results) was < 1.0%. This translates into over 99% operational confidence levels for the derived model and 0.99 dependency coefficient of the inhibition efficiency on current density and inhibitor concentration. The correlation coefficients between values of inhibition efficiency and current density & inhibitor concentration from model-predicted results were all >98%.

Key words: Computation - Inhibition efficiency - White starch - Mild steel corrosion - Sulphuric acid

INTRODUCTION

Corrosion attack on industrial facilities has resulted to loss of large sums of money following structural failures of these facilities due to the attack.

Naturally, degradation of metal and alloy as a result of environment surrounding them is unavoidable and can never be completely overcome but can be hindered or controlled to a reasonable extent through the use of some macromolecules [1-10], organic compounds [11-16] or extracts from natural plants [17-23] as corrosion inhibitors.

Macromolecules are polymeric in nature; formed by the repetition of smaller molecules (monomers) that are covalently bonded together. They are widely used as binders and thickeners in surface coating, dyes,

pigments following the ease with which the physical and chemical properties of the polymer are processed and modified. They can also be used as plastics, textile materials, rubber, adhesives and drilling mud. Biodegradability, non-toxicity, readily availability, low cost, renewability, water solubility are some of the inherent properties of the polymer (natural and synthetic) which raised its global acceptability in controlling corrosion of metals and alloys in various aggressive environments. Multiple functional and substituent groups either in their back bone or side chains are prime determining factors in the preferment of polymers and their blends over simple organic compounds as inhibitors for corrosion control. This is because presence of the highlighted groups at the back bone or side chains acts as regions at which electrons

are donated or accepted from surface charge on the metal. Studies [24-27] have shown that some organic compounds are effective corrosion inhibitors due to presence of hetero-atoms (nitrogen, sulphur, oxygen, etc.) combination of the atoms in their molecular structures. Research [28] has shown that polymers function as effective corrosion inhibitors even at low concentrations by forming complexes through their multiple functional and substituent groups with the metal ions which are adsorbed on metal surface and formed protective films at interface between metal and aggressive solution [29]. It is strongly believed that the inhibitive performance of polymers is a function of the molecular structure and solubility parameter of the polymers in various solvents of exposure.

Recently, concern has been raised on research and development directed towards the utilization eco-friendly polymers in controlling of metal corrosion in acid induced environment in attempt to protect our environment, safe guard human life, save our economy and reduce the material loss. Among the eco-friendly polymers used in controlling metal corrosion in aggressive media, starch which is a biopolymer has not found wide applicability [30-32] in the field of corrosion science despite the different sources of starch.

Scientists [33] have investigated the corrosion of mild steel in 0.5 M H₂SO₄ acid solution and the inhibition process by wheat starch (WS) using weight loss and potentiodynamic polarization measurement techniques respectively. Gravimetric results revealed that there is significant reduction in the corrosion rate of mild steel in the presence of inhibited solution compared to blank solution. Evaluations indicate that the inhibition efficiency was dependent on the concentration of the WS. Results from potentiodynamic polarization on firmid that WS exhibited mixed type inhibition behaviour, though the cathodic effect was more pronounced. The mode of WS adsorption on the corroding metal surface followed Langmuir isotherm model. In addition, the trend of inhibition efficiency with temperature, activation energy and heat of adsorption parameters revealed a strong interaction between the WS constituents and the corroding metal surface. This indicates that WS lowered the corrosion process by blanketing the mild steel surface through chemical adsorption mechanism.

The present research presents a computational analysis of the inhibition efficiency of white starch on mild steel corrosion based on current density and inhibitor concentration.

MATERIALS AND METHODS

Materials Preparation: The mild steel sheet (with percentage composition of C = 0.06, Si = 0.03, Mn = 0.04, Cu = 0.06, Cr = 0.06, and remainder Fe) was mechanically press-cut into coupons of dimension, 3cm x 4cm x 0.1cm. The coupons were degreased in absolute ethanol, dried in acetone and warm air and subsequently stored in moisture-free desiccators prior to use [33].

Test Solutions: Sulphuric acid used was of BDH AR grade. Other reagents (Sodium hydroxide, acetone and ethanol) used for the research were of Analar grade and double distilled water was used for preparation of blank and inhibited solutions. The blank corrodent was 0.5 M H₂SO₄ solution. The inhibitor; wheat starch (WS) used was processed using a method as in [33]. Test solutions of the WS were prepared in the concentration range 0.2-0.8 g/L.

Weight Loss Experiment: The cleaned and weighed coupons were suspended using glass hooks and rods in beakers containing 200ml test solutions. All experiments were performed under total immersion conditions of the aerated and unstirred test solutions at room temperature (30±1°C). Weight loss was determined with respect to time by retrieving the coupons from test solutions, cleaned, dried, and reweighed respectively at 24 hours intervals progressively for 5 days. The difference between the weight of the coupons at a given time and its initial weight was taken to be weight loss. All tests were run in triplicate to obtain good reproducibility data and average values for each experiment obtained were used in subsequent calculations. The value of corrosion rate was determined using the equations [33].

$$CR \text{ (mm/yr)} = \frac{87.6 \times 103 \Delta W}{\rho A t} \quad (1)$$

where ΔW is the weight loss in gram (g), ρ is the density of the mild steel coupons (g/cm³), t is the time of exposure (h) and A is the exposed surface area of the coupons (cm²). The percentage inhibition efficiency η (%) was calculated as in [33]:

$$\eta \text{ (%) } = \left[1 - \left(\frac{CR_{inh}}{CR_{blank}} \right) \right] \times 100 \quad (2)$$

where CR_{inh} is the corrosion rate in the presence of inhibitor and CR_{blank} is the corrosion rate in absence of inhibitor.

Potentiodynamic Polarization Measurements: The potentiodynamic polarization measurements were performed in a computer controlled electrochemical workstation (PARC- 263 model). The experiments were carried out in a cylindrical glass electrolytic corrosion cell with graphite rod as counter electrode (CE), saturated calomel electrode (SCE) as reference electrode (RE) and metal coupon as the working electrode. The working electrode was immersed in the test solution and allowed to corrode freely for 30 min to attain open circuit potential (OCP). The potentiodynamic polarization results were obtained in the potential range of $\pm 250mV$ versus corrosion potential using linear sweep technique at a scan rate of $0.333mV/s$. All the measurements were carried out at room temperature ($30\pm 1^\circ C$). The potentiodynamic polarization data was used to extrapolate the data using Power suite software.

Each test was run in triplicates to verify the reproducibility of the system. The inhibition efficiency was calculated as in [33]:

$$\eta_{corr} (\%) = \left(1 - \left(\frac{i_{corr}^1}{i_{corr}^2} \right) \right) \times 100 \quad (3)$$

where i_{corr}^1 is the corrosion current in the presence of inhibitor whereas i_{corr}^2 is the corrosion current in the absence of inhibitor.

RESULTS AND DISCUSSION

Table 1: Variation of inhibition efficiency η with current density i_{corr} and inhibitor concentration ϑ [23]

(η)	(i_{corr})	(ϑ)
84.32	124.23	0.2
88.06	87.06	0.4
89.06	79.06	0.6
90.61	68.16	0.7
92.15	57.24	0.8

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

$$\eta - K = \beta \ln \vartheta - N \ln i_{corr} \quad (4)$$

Introducing the values of K, β and N into equation (4) reduces it to;

$$\eta - 113.1 = 2.6 \ln \vartheta - 5.1 \ln i_{corr} \quad (5)$$

$$\eta = 2.6 \ln \vartheta - 5.1 \ln i_{corr} + 113.1 \quad (6)$$

where,

$K = 113.1$, $\beta = 2.6$ and $N = 5.1$; equalizing constant (determined using C-NIKBRAN [34])

(η) = Corrosion inhibition efficiency (%)

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

(i_{corr}) = Current density (μAcm^{-2})

Boundary and Initial Conditions: Consider short cylindrically shaped mild steel coupon submerged in sulphuric acid, interacting with some corrosion-induced agents. The solution is assumed to be affected by undesirable dissolved gases. The considered range of the current densities, inhibitor concentrations and inhibition efficiencies are $57.24-124.23 (\mu A cm^{-2})$, $0.2-0.8 (g/l)$ and $84.24- 92.15 (\%)$ respectively.

Table 2: Variation of $\eta - K$ with $\beta \ln \vartheta - N \ln i_{corr}$

$\eta - K$	$\beta \ln \vartheta - N \ln i_{corr}$
- 28.78	- 28.78
- 25.04	- 25.16
- 24.04	- 23.62
- 22.49	- 22.46
- 20.95	- 21.22

Model Validity: The validity of the model is strongly rooted on the core model equation (4) where both sides of the equation are correspondingly almost equal. Table 2 also agrees with equation (4) following the values of $\eta - K$ and $\beta \ln \vartheta - N \ln i_{corr}$ evaluated from the actual results in Table 1. Furthermore, the derived model was validated by comparing the inhibition efficiencies 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.

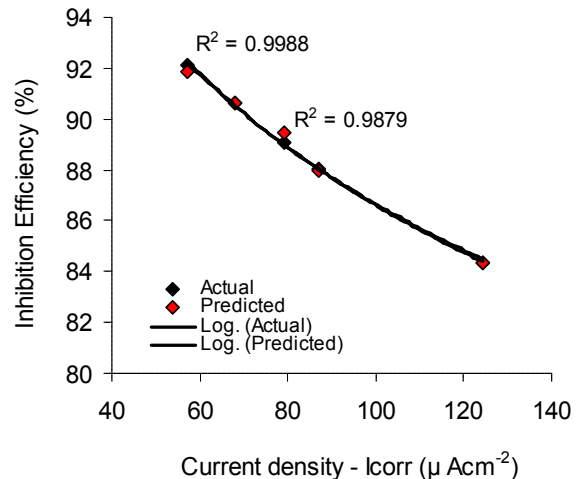


Fig. 1: Coefficient of determination between inhibition efficiency and current density as obtained from actual and model-predicted results

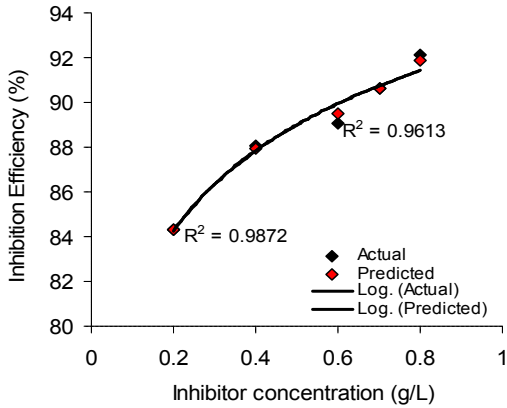


Fig. 2: Coefficient of determination between Inhibition efficiency and concentration of inhibitor as obtained from actual and model-predicted results

Computational Analysis:

Inhibition efficiency per unit inhibitor concentration.

Inhibition efficiency per unit inhibitor concentration η_{-g} , (%/ (g/l)), was calculated from the equation;

$$\eta_{-g} = \eta / g \tag{7}$$

Re-written as

$$\eta_{-g} = \Delta\eta / \Delta g \tag{8}$$

Equation (8) is detailed as;

$$\eta_{-g} = \frac{\eta_2 - \eta_1}{g_2 - g_1} \tag{9}$$

where

η_{-g} = Change in the inhibition efficiencies η_2 , η_1 at inhibitor concentrations g_2 , g_1 .

Considering the points (0.2, 84.32) & (0.8, 92.15) and (0.2, 84.32) & (0.8, 91.88) as shown in Fig. 2, designating them as (η_1, g_1) & (η_2, g_2) for actual and model-predicted results, and then substituting them into equation (9), gives the slopes: 13.05 and 12.60 % / (g/L) respectively as the inhibition efficiencies per unit inhibitor concentration. Results predicted by empirical model show that the inhibition efficiency increases with increase in inhibitor concentration and decreases in current density, line with previous work [24]. The decrease in the current density is an indication of reduction in corrosion attack on the mild steel.

Statistical Analysis

Correlation: The correlation coefficient between inhibition efficiency and current density & inhibitor concentration 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 (10). These results are 0.9994 and 0.9939 & 0.9805 and 0.9936, respectively.

$$R = \sqrt{R^2} \tag{10}$$

Standard Error (STEYX): The standard error incurred in predicting the model-based inhibition efficiency relative to values of the actual results is 0.29 %. The standard error was evaluated using Microsoft Excel version 2003.

Graphical Analysis: The validity of the derived model was further verified by plotting values of the actual, besides the model-predicted results using Microsoft Excel (version 2003) to evaluate the trend of both results. Comparative analysis of Figs. 3 and 4 indicate very close alignment of curves which depicted significantly similar trend of data point’s distribution for the actual and derived model-predicted inhibition efficiency. This shows proximate agreement between both results.

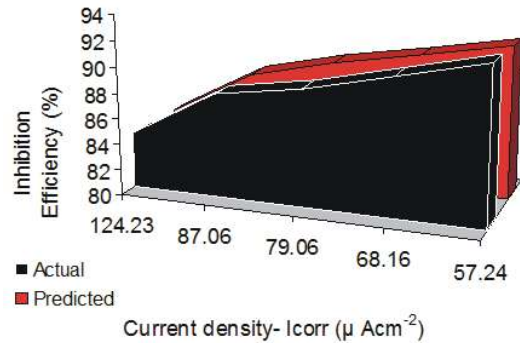


Fig. 3: Variation of inhibition efficiencies with current density as obtained from actual and model-predicted results

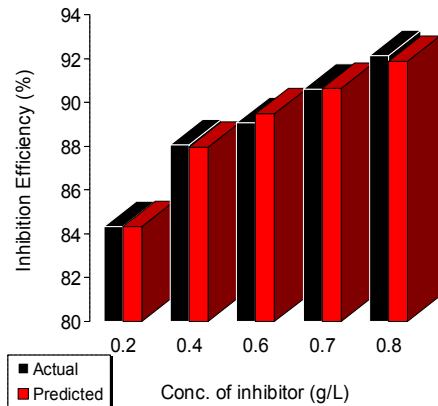


Fig. 4: Variation of inhibition efficiencies with inhibitor concentration as obtained from actual and model-predicted results

Deviational Analysis: Analysis of the inhibition efficiencies obtained from the actual and model-predicted results show insignificant deviation between actual and the 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 sulphuric acid were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted inhibition efficiency to those of the corresponding experimental values.

The deviation Dv , of model-predicted inhibition efficiency from the corresponding actual result was given by;

$$Dv = \left(\frac{\eta_P - \eta_E}{\eta_E} \right) \times 100 \quad (11)$$

where

η_E and η_P are inhibition efficiencies evaluated from actual and model-predicted respectively.

Fig. 5 shows that maximum deviation of model-predicted inhibition efficiency from the actual results was less than 0.5 %. This translates into over 99% model operational confidence. The figure shows that the least and highest deviations of model-predicted results (from actual results) are 0% and 0.47 %.

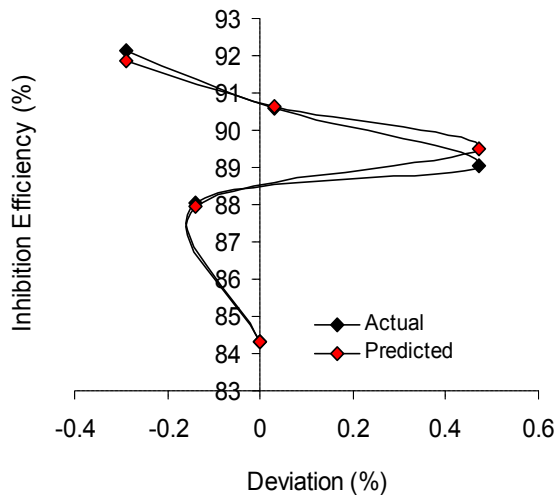


Fig. 6: Deviation of model-predicted results from actual values

These deviations correspond to model-predicted inhibition efficiencies: 84.32 and 89.48 (%), current densities: 124.23 and 79.06 (μAcm^{-2}), inhibitor concentrations: 0.2 and 0.6(g/L) respectively.

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

$$Cf = - \left(\frac{\eta_P - \eta_E}{\eta_E} \right) \times 100 \quad (12)$$

Critical analysis of Fig. 5 and Fig.6 show that the evaluated correction factors are negative of the deviation as shown in equations (11) and (12).

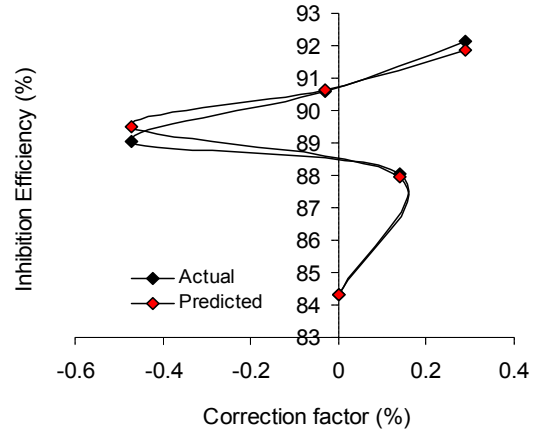


Fig. 6: Correction factor to model-predicted results

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 (12) into the model gives exactly the corresponding actual inhibition efficiency. Fig. 6 indicates that the maximum correction factor to the model-predicted current density was less than 0.5 %. The figure shows that the least and highest correction factors to the model-predicted results (from actual results) are - 0 and - 0.47%. These correction factors also correspond to model-predicted inhibition efficiencies: 84.32 and 89.48 (%), current densities: 124.23 and 79.06 (μAcm^{-2}), inhibitor concentrations: 0.2 and 0.6 (g/L) respectively.

The negative and positive signs preceding numerals in reported deviation and correction factors merely indicate deficit and surplus respectively. The actual deviation or correction factor is just the numeral.

CONCLUSION

Computational analysis of the inhibition efficiency of white starch on mild steel corrosion in 0.5 M H_2SO_4 based on current density and inhibitor concentration was carried out. A derived empirical

model; $\eta = 2.6 \ln i - 5.1 \ln i_{\text{corr}} + 113.1$ computes the corrosion inhibition efficiency of the white starch as subtraction of two natural logarithmic parts involving inhibitor concentration and current density. Results predicted by the model show that inhibition efficiency increases with increase in inhibitor concentration and decrease in the current density, in line with previous work. The decrease in the corrosion current density is an indication of reduction in corrosion attack on the mild steel. The validity of the model was rooted on the core model expression $\eta - K = \ln i - \ln i_{\text{corr}}$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based inhibition efficiency relative to the actual results was 0.29%. Evaluations from generated results indicate that the inhibition efficiency per unit inhibitor concentration as obtained from the actual and model-predicted results are 13.05 and 12.60 % / (g/L) respectively. Maximum deviation of model-predicted results (from actual results) was < 1.0%. This translates into over 99% operational confidence levels for the derived model and 0.99 dependency coefficient of the inhibition efficiency on current density and inhibitor concentration. The correlation coefficients between values of inhibition efficiency and current density & inhibitor concentration from model-predicted results were all > 98%.

REFERENCES

1. Bereket, G.A., A. Yurt and H. Turk, 2003. Inhibition of corrosion of low carbon steel in acidic solution by selected polyelectrolytes and polymers, *Anti-Corrosion Methods Mater*, 50: 422-535.
2. Daouadji, M.M, and N. Chelali, 2004. Influence of molecular weight of poly (ortho-ethoxyaniline) on the corrosion inhibition efficiency of mild steel in acidic media, *J. Appl. Polym. Sci.*, 91:1275-1284.
3. Selvaraji, S.K., *et al.*, 2004. Corrosion behaviour of carbon steel in the presence of polyvinylpyrrolidone, *Corrosion Rev.*, 22: 219-232.
4. Manickavasagam, R., *et al.* 2002. Poly(styrene sulphonic acid) doped polyaniline as an inhibitor for the corrosion of mild steel in hydrochloric acid, *Anti-Corrosion Methods Mater*, 49(1):19-26.
5. Morooka, M., *et al.*, 2001. Effects of polymer-polymer complexes on the corrosion of mild steel in cooling water system (part 2): corrosion investigation in polymethacrylic acid/ polyacrylamide system, *Corrosion Eng.*, 50:106-114.
6. Jianguo, J., *et al.*, 1995. Polyvinylpyrrolidone and polyethylenimine as corrosion inhibitors for the corrosion of a low carbon steel in phosphoric acid, *Corrosion Sci.*, 37:975-985.
7. Dubey, A.K. and G. Singh, 2007. Corrosion inhibition of mild steel in sulphuric acid solution by using polyethylene glycol methyl ether (PEGME), *Port. Electrochim. Acta.*, 25(2): 221-235.
8. Umore, S.A., *et al.*, 2006. Water soluble polymers as corrosion inhibitors of mild steel in acidic medium, *Pigment and Resin Technol.*, 35(6): 346-352.
9. Umoren, S.A. and I.B. Obot, 2008. Polyvinyl pyrrolidone and polyacrylamide as corrosion inhibitors for mild steel in acidic medium, *Surf. Rev. Lett.*, 25: 277-284.
10. Nwanonyi, S.C., *et al.*, 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.
11. Shibli, S.M.A. and V.S. Saji, 2005. Co-inhibition characteristics of sodium tungstate with potassium iodide on mild steel corrosion, *Corrosion Science*, 47:2213-2224.
12. Oguzie, E.E., G.N. Onuoha and A.I. Onuchukwu, 2005. Inhibitory mechanism of mild steel corrosion in 2M sulphuric acid solution by methylene blue dye, *Mater. Chem. Phys.*, 89: 305-311.
13. Oguzie, E.E., *et al.*, 2004. Inhibition of mild steel corrosion in sulphuric acid using indigo dye and synergistic halide additives, *Mater. Chem. Phys.*, 84: 363-368.
14. Larabi, L., *et al.*, 2005. Erratum to Hydrazide derivatives as corrosion inhibitors for mild steel in 1 M HCl, *Prog. Org. Coat.*, 54:256-262.
15. Xia, S., *et al.*, 2008. Molecular dynamics and density functional theory study on relationship between structure of imidazoline derivatives and inhibition performance, *Corros. Sci.*, 50: 2021-2029.
16. Shaker, M.A. and H.H. Abdel-Rahman, 2007. Corrosion of copper metal in presence of binary mixtures, *Am. J. Appl. Sci.*, 4: 554.
17. Singh, A., *et al.*, 2011. Inhibition effect of environmentally benign *Karanj (Pongamia pinnata)* seed extract on corrosion of mild steel in hydrochloric acid solution, *Journal of Solid State Electrochemistry*, 15: 1087-1097.

18. Mejeha, I.M., *et al.*, 2010. The inhibitive effects of *Solanum melongena* L. leaf extract on the corrosion of aluminium in tetraoxosulphate (VI) acid, *Afr. J. Pure Appl. Chem.*, 4(8): 158-165.
19. Chidiebere, M.A., *et al.*, 2012. Corrosion inhibition and adsorption behavior of *Punica granatum* extract on mild steel in acidic environments: Experimental and theoretical studies, *Ind. Eng. Chem. Res.*, 51:668-677.
20. Oguzie, E.E., 2005. Inhibition of acid corrosion of mild steel by *Telfaria occidentalis* extract, *Pigm. Resin Technol.*, 34(6):321-326.
21. Obot, I.B., Z.M. Gasem and S.A. Umoren, 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.
22. Nwanonenyi, S.C., *et al.*, 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.
23. Nwanonenyi, S.C., *et al.*, 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.
24. Shokry, H., *et al.*, 1998. Corrosion inhibition of mild steel by schiff base compounds in various aqueous solutions: part 1, *Corrosion Science*, 40: 2173-2186.
25. Yurt, A., *et al.*, 2004. Investigation of schiff bases as HCl corrosion inhibitors for carbon steel, *Mater. Chem. Phys.*, 85:420-426.
26. Granese, S.L., 1988. Study of the inhibitory action of nitrogen containing compounds, *Corrosion.*, 44:322-327.
27. Tadros, A.B. and B.A. Abd El-Nabey, 1988. Inhibition of the acid corrosion of steel by 4-amino-3-hydrazino-5-thio-1,2,4-triazoles, *Journal of Electro analytical Chemistry and Interfacial Electrochemistry*, 246:433-439.
28. Banerjee, S., *et al.*, 2011. Highly efficient polyurethane ionomer corrosion inhibitor: the effect of chain structure, *RSC Advances.*, 1:199-210.
29. Rajendran, S., *et al.*, 2005. Corrosion behaviour of carbon steel in polyvinyl alcohol, *Anti-Corrosion Methods Mater.*, 52:102-107.
30. Bello, M., N. Ochoa and V. Balsamo, 2011. Effect of the environmental pH on the corrosion bio inhibitive properties of modified cassava starches, in: *Proceedings of the 69th Annual Technical Conference & Exhibition*, Boston, pp: 266.
31. Charitha, B.P. and P. Rao, 2017. Starch as an eco friendly green inhibitor for corrosion control of 6061-Al alloy, *J. Mater. Environ. Sci.*, 8(1): 78-89.
32. Arthur, D.E., *et al.*, 2013. A review on the assessment of polymeric materials used as corrosion inhibitor of metals and alloy, *International Journal of Industrial Chemistry*, 4(2): 1-9.
33. Nwanonenyi, S.C., O. Ogbobe and E.E. Oguzie, 2017. Protection of mild steel corrosion in sulphuric acid environment using wheat starch. *International Journal of Engineering and Technologies*, 10: 11-21.
34. Nwoye, C.I., 2008. *Data Analytical Memory; C-NIKBRAN.*