Research Journal of Applied Sciences, Engineering and Technology 17(2): 40-53, 2020
DOI:10.19026/rjaset.17.6038
ISSN: 2040-7459; e-ISSN: 2040-7467

Submitted: July 15, 2019 Accepted: September 03, 2019 Published: April 15, 2020

Research Article

Thermodynamic, Adsorption and Optimization Studies on Carbon Steel in Hydrochloric Acid Environment using Okro Leaf Extract as Corrosion Inhibitor

[1]A.O. Okewale, [1]C.N. Owabor and [2]J.G. James
[1]Department of Chemical Engineering, Federal University of Petroleum Resources,
[2]Department of Petroleum and Natural Gas Processing Engineering, Petroleum Training Institute,
Effurun, Delta State, Nigeria

Abstract: This present study seeks to exploit the use of eco-friendly, Okro leaf extract as an inhibitor in mitigating corrosion on carbon steel metal in acidic environment Gravimetric method was used to study the corrosion process. It was revealed that the inhibition efficiency of the extract on carbon steel decreases as temperature increases. This trend confirmed the physical adsorption mechanism for the corrosion process that resulted in a high rate of corrosion of the carbon steel. Activation energy Ea, enthalpy (ΔH°), and entropy (ΔS°) calculated showed good interactions. The rise in activation energy with inhibitor concentration confirmed the physical (physisorption) adsorption mechanism for the corrosion of a carbon steel surface. The positive value of adsorption enthalpy (ΔH°) obtained confirmed the endothermic nature of the corrosion process. The activation entropy (ΔS°) values obtained were all negatives which show that the activated complex in the rate-determining step represents association rather than dissociation step. Corrosion inhibition occurred by an attribute of inhibitor molecules adsorption on the surface of carbon steel which is seen to be in conformity with Langmuir, Freundlich, and El-Awady adsorption isotherm models. To obtain the least weight loss of carbon steel, optimization of the process variables affecting the corrosion process was carried out using Response Surface Methodology (RSM). Three parameters were varied viz; inhibitor concentration, contact time and temperature, and their effects on weight loss of carbon steel were established. The obtained data fitted well to the quadratic model which was also validated. The model predicted the lowest weight loss of 0.045 g with the optimal condition of inhibitor concentration of 198.71 ppm, 2.04 hrs of contact time, and 40.29°C of temperature.

Keywords: Adsorption, inhibition, okro leaf extract, optimization, RSM, thermodynamic

INTRODUCTION

The consequences of corrosion are numerous, diverse and effects of these on the efficient, safe and reliable operation of equipment or edifices are often more serious than simple loss of a mass of metal. In reality, corrosion can never be stopped but can be hindered to a reasonable level.

Failure of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small (Umoren *et al*., 2009). The phenomenon of corrosion mitigation, abatement and inhibition are major scientific issues that should be tackled daily due to the increasing need for metallic materials in the technological advancement of our industries. Owing to harms arising from corrosion that are challenging the chemical and process industries; several methods of controlling corrosion and prevention have been put in place. Some of these methods include; anodic and cathodic protection, lubrication, galvanizing, alloying, coating and the use of organic and inorganic inhibitors. The choice and application of any of these methods was based on their economic factors, efficiency and nature of the corrosive environment (Njoku, 1998). The use of inhibitor is one of the most practical methods for protection against corrosion in corrosive environments. Inhibitors are chemicals that directly or indirectly coat a film on a metal surface to protect it from its environment. Generally, inhibitors are absorbed by the metal surface from a solution or dispersed, but some are applied directly as coatings. However, the dissolution of metal can be suppressed by the action of adsorptive inhibitors which may prevent the adsorption of the aggressive ions and by the formation of a more resistant film on the metallic surface (El Maghraby, 2009). Historically,

Corresponding Author: A.O. Okewale, Department of Chemical Engineering, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria

most of the known corrosion inhibitors are synthetic chemicals (heavy metal), expensive and very hazardous to environment.

Therefore, it is desirable to source for environmentally safe inhibitors (Paul *et al*., 2012). In view of these, researches had been undertaken on the development of an ecofriendly natural inhibitors and one of such is Okro leaf (*Abelmoschus esculentus*). The Okro leaf phytochemical is rich in tannins, steroids, flavonoids, phenols and terpenoids (Dheba *et al*., 2017). These phytochemical constituents especially tannins have an array of hydroxyl and carboxyl groups through which the molecules can adsorbed on corroding metallic surfaces thus inhibiting the corrosion process on the carbon steel (Oki *et al*., 2011).

Optimization and modeling is of great importance in any process as it improves the yield (Adepoju and Eyiobi, 2016). The use of a unity variable method for modeling and optimization is now becoming outdated because it does not show any interaction between the other variables considered in the process (Seramen *et al*., 2010). Response Surface Methodology (RSM) is a method of optimization which consists of experimental design, analysis and modeling through the partial fitting of regression from the experimental factors (Wang *et al*., 2011). RSM has the ability to link many variables at a time and display the mutual interaction on the yield of a route, it also facilitate reduction in the amount of experimental runs required to provide adequate evidence for results that are acceptable statistically. Extract from leaves has been studied as a potential for corrosion inhibitor but no research has been conducted on the use of Okro leaf extract as a corrosion inhibitor. Likewise, RSM has not been reported on corrosion inhibition of carbon steel using Okro leaf extract.

This present work studied the Okro leaf extract as an inhibitor, kinetics and mechanism of adsorption and also optimized the process variables already reported in literature affecting corrosion process (Yawas, 2005). In order to minimize the weight loss of the carbon steel, RSM was used to know the effects of three factors (temperature, concentrations and contact time) and their reciprocal effect on rate of corrosion on carbon steel metal. The work established the process condition in a view to achieving minimum weight loss on carbon steel which could be applied to local and industrial corrosion treatment.

MATERIALS AND METHODS

The okro leaves (*Abelmoschus esculentus)* were collected from Agbahro community located in Effurun, Delta State, Nigeria. Soxhlet extractor apparatus (Techmel and Techmel, USA), oven (Gallenkamph 2), PGW752i weighing balance with resolution of 0.001 mg were used for the study.

Okro leaf extract preparation: The Okro leaves (*Abelmoschus esculentus)* were washed thoroughly with running water to remove unwanted materials. The washed samples were dried in open air for 4 days and grinded to a particle seize of 0.143 μm. The sample was stored in a desiccator before used. 25 g of the dried alligator pepper pods powder was transferred into a 500 mL round-bottom flask and 300 mL of 70% ethanol. A reflux condenser was then connected to the flask and cold water was allowed to flow through the condenser for better reduction of solvent losses. The set-up was placed on a heating mantle and the Okro leaf extract was extracted exhaustively by heating the solution under reflux at 78°C. Rotary evaporator (model R-210) was used to remove the remaining solvent (ethanol) from the extract.

Procedure of the experiment: The gravimetric or weight loss method was used. The carbon steel was mechanically polished with silicon carbide abrasive paper, degreased with ethanol, washed in distilled water and dried in acetone. Each carbon steel coupon was sized 40 mm×20 mm×2 mm. Before polishing, a hole of 0.1 cm was drilled on each coupon. The coupon was suspended with the aid of a nylon thread in a 100 mL beaker with 100 mL of 1.5M HCl at different inhibitor concentrations.

The mechanism of inhibition and thermodynamic parameters were studied at 308, 318, 328, 338 and 348 K temperature at contact time of 7 h. Each of the carbon steel metal coupons after the corrosion process was dipped in both distilled water and ethanol solutions. This was scrubbed to remove any remaining residual inhibitor concentration and HCl. Thereafter, the coupon was then washed thoroughly with washing liquor, rinsed with distilled water and later dried in acetone before been reweighed.

Determination of weight loss: The weight loss of the mild steel coupon was determined using Eq. (1):

$$\text{Weight loss, (g)} = W - W_i \quad (1)$$

where,

W = The initial weight of the mild steel coupon

W_i = The weight of the carbon steel coupon after corrosion study

Determination of inhibitor efficiency: The efficiency of corrosion inhibition was obtained using the equation below:

$$E(\%) = \frac{W_b - W_c}{W_b} \times 100 \quad (2)$$

where,

W_b = The loss in weight in uninhibited medium (blank)

W_c = The loss in weight in inhibited medium

Optimization studies on rate of corrosion on carbon steel: Optimization of the process variables influencing the rate of corrosion was carried out using Response

Table 1: Experimental factors codes and level

Variables	Symbol	Low factor (-1)	Mid-point factor (0)	High factor (+1)
Concentration of inhibitor, (ppm)	X_1	50	150	250
Contact time, (hr)	X_2	2	7	12
Temperature, (°C)	X_3	35	45	55

Surface Methodology (RSM). Three variables were varied viz; concentration of Okro leaf extract (inhibitor), temperature and contact time and their effects on weight loss of the carbon steel was investigated. 17 experiments runs were generated using the Box Behnken Design (BBD). The model fitness was evaluated using test of significance and Analysis of Variance (ANOVA). The selected factors concentration of inhibitor, contact time and temperature represent X_1, X_2 and X_3 respectively. This is shown in Table 1.

The coefficient of the polynomial model was determined using the multiple regressions as shown in Eq. (3):

$$Y = b_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j} \beta_{ij} X_i X_j + e \quad (3)$$

where,
Y = The weight loss
b_o = The intercept
b_{ij} = The interaction effect
b_{ii} = The quadratic coefficients of X_i
e = The random error

(Omoruwou *et al*., 2017; Betiku and Adesina, 2013). Design Expert 7.00 software was used to design and analyze the data from the experiment. This is a statistical software package that does design of experiments, comparative tests and optimization of the process variables. It is also used to study the parameters on the yield of a process using the graphical tool.

RESULTS AND DISCUSSION

As evidenced in Table 2, the preponderance of tannin, flavonoids, steroids, phenols and terpenoids in the Okro leaf Extract can be said to enhance the corrosion inhibition of carbon steel in acidic environment studied. The presence of these compounds has been reported to promote the corrosion inhibition of mild steel in aggressive acidic media (Umoren *et al*., 2006). This also corroborates the work of Prithiba *et al*. (2014), Owate *et al*. (2014) and Nwigbo *et al*. (2012).

Effect of temperature of corrosion rate of carbon steel: Figure 1 present the effect of temperature on rate of corrosion of carbon steel. It can be seen that the rate of corrosion is higher in medium without inhibitor in comparison to the one that has inhibitor. Increased in temperature led to increase in corrosion rate of the carbon steel due to the fact that at higher temperature the process of corrosion occurred rapidly due to weakening of the adsorption capacity of the inhibitor due to the hot-movement of inhibitor molecules from the metal surface. The obtained result is in agreement with reports of (Shivakumar and Mohana, 2012; Norzila and Ishak, 2015).

Table 2: Phytochemical analysis of Okro leaf extract (*Abelmoschus esculentus*)

Chemical components	Plant extracts
Tannins	+++
Steriods	+++
Flavonoids	+++
Saponins	+
Alkaloids	+
Anthraquinones	+
Phenols	+++
Resin	++
Terpenoids	+++
Cardiac Glycosides	+++

+++ = Rich, ++ Moderate, + = good, - = Absent, Dheba *et al*., (2017)

Temperature effect on inhibition efficiency: The inhibition efficiency of the inhibitor for the carbon steel decreases with increasing temperature, a trend that confirm physical adsorption mechanism for the corrosion process that is caused by desorption of adsorbed inhibitor as a result of higher rate of hydrogen evolution due to increased agitation of solution brought by higher temperature. This is similar to the result obtained by Abd El-hameed (2011) (Fig. 2).

Thermodynamics and adsorption studies: Thermodynamic properties such as Activation Energy (Ea), Enthalpy (ΔH°) and Entropy of Activation (ΔS°) were undertaken so as to ascertain the mechanism of adsorption process involved in the carbon steel corrosion process. In order to calculate the thermodynamics parameters like enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) of corrosion process in the presence and absence of Okro leaf extract inhibitor in hydrochloric acid solution the transition state theory equation given by Eq. (4) was used (Alhaffar *et al*., 2018; Ogoke *et al*., 2009):

$$log\left(\frac{C_R}{T}\right) = \left[log\left(\frac{R}{Nh}\right) + \frac{\Delta S^o}{2.303R}\right] - \frac{\Delta H^o}{2.303RT} \quad (4)$$

where, h is the Planck's constant (6.626176×10^{-34}Js), N is the Avogadro's number, (6.022×10^{23} mol^{-1}), R is the Universal gas constant (8.314 J/Kmol) and T is the temperature of the medium. The plot of $log(C_R/T)$ against 1/T is seen to be linear in Fig. 3 from which (ΔH°) and (ΔS°) values were calculated from the slopes

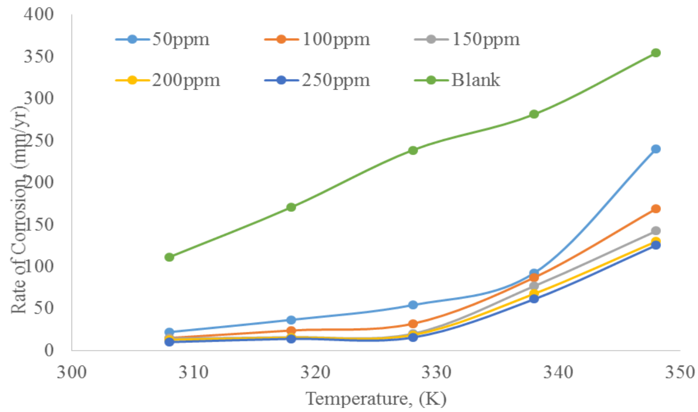

Fig. 1: Effect of temperature of corrosion rate of stainless steel

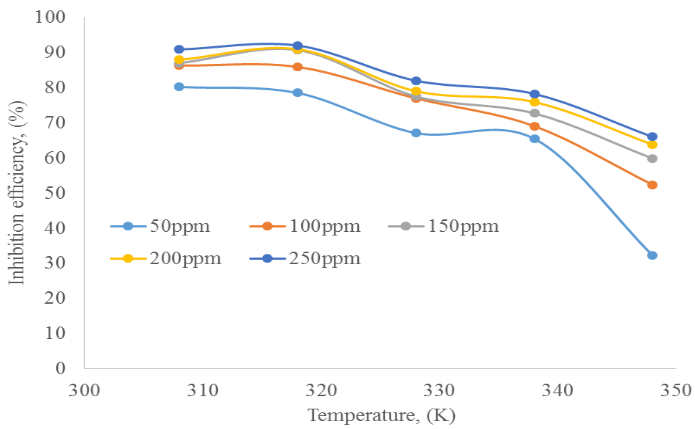

Fig. 2: Effect of temperature on corrosion inhibition efficiency

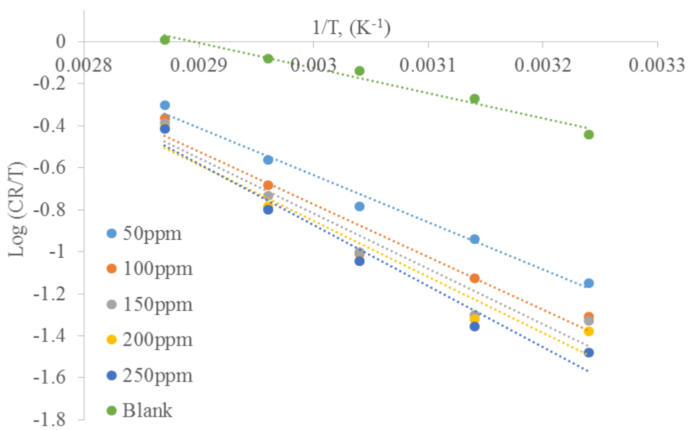

Fig. 3: Transition state plot for the corrosion inhibition of carbon steel

Table 3: Thermodynamics parameters for carbon steel in the presence and absence of inhibitor

Concentration of Inhibitor	Ea (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
Blank	25.62	22.89	-131.29
50 ppm	51.27	42.94	-80.92
100 ppm	54.89	48.09	-68.09
150 ppm	54.55	50.47	-61.86
200 ppm	54.16	50.97	-61.00
250 ppm	57.93	55.69	-47.28

and intercept of the graph respectively and listed in Table 3. Arrhenius equation given by Eq. (5) was used to calculate the activation energy E_a in the presence and absence of Okro leaf extract inhibitor:

$$\log C_R = \log A - \frac{E_a}{2.303RT} \quad (5)$$

where,

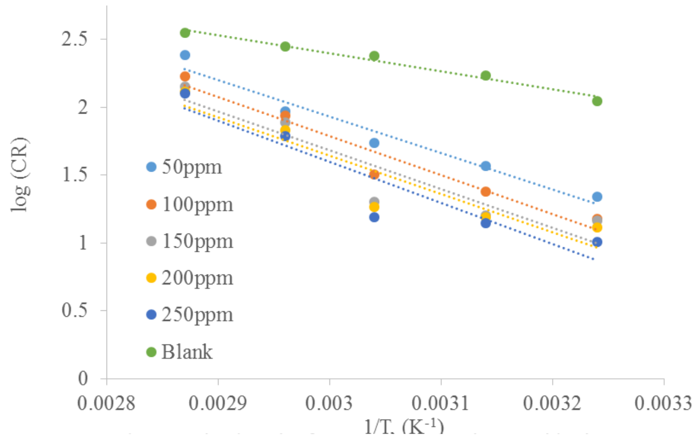

Fig. 4: Arrhenius plot for corrosion of carbon steel in the presence and absence of inhibitor

C_R = The rate of corrosion
Ea = The apparent activation energy
R = The universal gas constant
T = The absolute temperature
A = The frequency factor

The Arrhenius plot of log C_R against reciprocal of absolute temperature (1/T) is shown in Fig. 4 which gives a straight line with slope of -Ea/2.303 R from which the activation energy of the corrosion process was determined and listed in Table 3.

Table 3 shows the value of activation parameters obtained in this study. It can be seen that the values of corrosion enthalpy of adsorption (ΔH_{ads}) increased with inhibitor concentration of Okro leaf extract. The enthalpy of activation (ΔH°) values in the presence and absence of inhibitor are positive. From literature, the negative sign of (ΔH°) has been clearly associated with an exothermic adsorption process that can either be physisorption or chemisorption or combination of both. However, the positive sign is connected to endothermic adsorption process which is credited to physisorption. The positive sign of the enthalpy of activation as obtained in the present study reflects the endothermic nature of the process of carbon steel dissolution. This supposition is in conformity with the observed decrease in inhibition efficiency with temperature showing the physisorption of the inhibitor on the carbon steel metal surface. It was also observed that as inhibitor concentration is increased the efficiency of inhibition also increased. The entropy of adsorption (ΔS_{ads}) values decreased with inhibitor concentration. The activation entropy (ΔS°) values in the absence and presence of Okro leaf extract inhibitor were all negatives.

This implied to mean that the activated complex in the rate determining step represents association rather than dissociation step, indicating that during the adsorption process, a decrease in the degree of orderliness takes place when moving to the activated complex from the reactants with increased in inhibitor concentration, the order of activated complex entangled in the rate determining step of the corrosion reaction becomes more dissociated (Alhaffar *et al*., 2018). Hence, disorderliness is decreased as reactants are transformed to activated complex.

The value of Ea (activation energy) in blank solution is 25.62 kJ/mol and rise as inhibitor concentration is increased from 50 ppm (51.28 kJ/mol) to 100 ppm (54.89 kJ/mol). This is due to the physical barrier produced by the adsorbed molecules on the surface of carbon steel. This will increase the least energy required for corrosion reaction to occurs. It was observed that at both concentrations of 150 ppm and 200 ppm the activation energy of corrosion is 54.55 kJ/mol and 54.16 kJ/mol respectively which showed a downward trend compared to 100 ppm concentration but this is not lower in comparison to that of the blank solution. It has been reported that lower Ea value in the presence of inhibitors in comparison to the blank is attributed to chemical adsorption (Solomon *et al*., 2010; Thirumoolan *et al*., 2014; Alhaffar *et al*., 2018). Since the reverse is the case in this study it can be said that the mechanism of corrosion can be ascribed to physical adsorption (physisorption). At inhibitor concentration of 250 ppm the activation energy value was increased to 57.93 kJ/mol. The corrosion reaction will be pushed away on the surface site and occurs at the uncovered parts of carbon steel when inhibitor is added in hydrochloric acid solution thus giving a higher value of Ea (Quraishi *et al*., 2010).

The trend of increasing Ea values with inhibitor concentrations has been reported by other researchers on studies on various plant extract such as jujube leaves (Sivakumar and Mohana, 2012), black pepper (Quraishi *et al*., 2010), sunflower leaves (Hui *et al*., 2012) and piper nigrum extract (Norzila and Ishak, 2015). In this study, the increasing values of Ea obviously showed a physical adsorption of inhibitor molecules on the surface carbon steel. Physical adsorption happens due to the electrostatic force between negatively charged metal surface and positive charged of organic species (Norzila and Ishak, 2015).

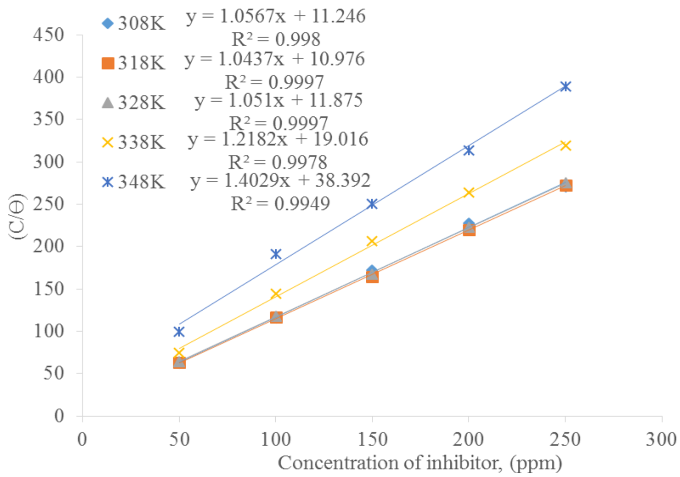

Fig. 5: Langmuir isotherm for adsorption of inhibitor on carbon steel surface

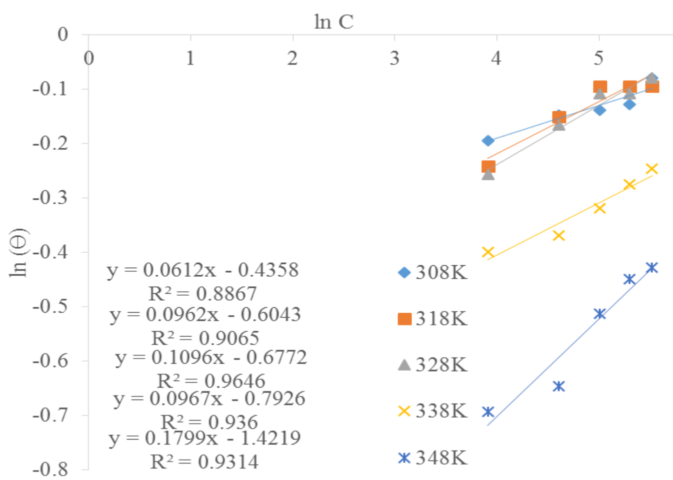

Fig. 6: Freundlich isotherm for adsorption of inhibitor on carbon steel surface

Adsorption isotherms: Four different adsorption isotherms were tested so as to obtain more knowledge about the interface between the carbon steel surface and inhibitor. The isotherms tested are Langmuir, Freundlich, Temkin and El-Awady adsorption isotherms. The linear regression coefficient of determination (R^2) was used to adjudge the model that best fit the experimental values.
Langmuir relationship is represented by Eq. (6):

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (6)$$

where, K is the equilibrium constant of adsorption (M^{-1}) which was employed to obtain the Gibb's free energy, C is the inhibitor concentration ppm and θ is the degree of surface coverage (Rajendran *et al.*, 2000; Nnanna *et al.*, 2014). A plot of C/θ against C as depicted in Fig. 5 gave a reciprocal of intercept as the adsorption constant. Using the K value determined from the Langmuir isotherm relationship, the standard Gibb's free energy of adsorption $\Delta G°_{ads}$ (kJ/mol) value at temperature range 35°C-75°C was determined according to Eq. (7) below:

$$\Delta G^{o}_{ads} = -RT\ln(55.5K) \qquad (7)$$

where,
R = The gas constant (8.314 J/mol)
T = The temperature (K)
55.5 = The standard molar of water in the solution (Cheng *et al.*, 2007)

Freundlich isotherm: The fitting of non-ideal system can be done sometimes by fitting the experimental data to Freundlich adsorption isotherm as in Fig. 12 (Yaro and Khadom, 2008). This is expressed in Eq. (8):

$$\theta = KC^{n} \qquad (8)$$

Equation 11 can be re-written as:

$$ln\theta = lnK + nlnC \qquad (9)$$

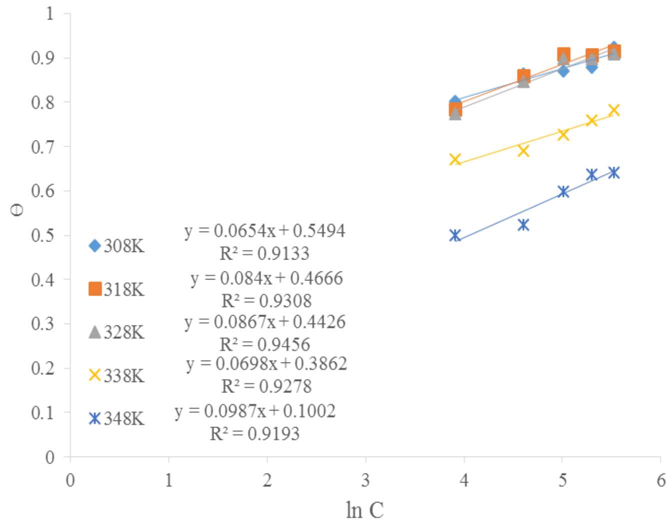

Fig. 7: Temkin isotherm for adsorption of inhibitor on carbon steel surface

A plot of ln θ against ln C should give a straight line as seen in Fig. 6. Where θ is the degree of surface coverage, C is the inhibitor concentration, in ppm, K is the adsorption constant which is a measure of adsorption capacity, (L/g) and n is the positive constant called the Freundlich exponent which talks about the intensity of adsorption process on the carbon steel surface.

Temkin isotherm: This is expressed in Eq. (10):

$$\Theta = \frac{1}{f}\ln(K_{ads}C) \qquad (10)$$

Equation 10 can be re-written as:

$$\Theta = \frac{1}{f} lnC + \frac{1}{f} lnK \qquad (11)$$

where, θ is a linear function of ln C (Nnanna *et al*., 2010), K is the equilibrium constant of adsorption, (L/g), C is the inhibitor concentration, (g/L) and f is a coefficient of inhomogeneity connected with the range of inhomogeneity C by Eq. (12):

$$f = C/RT \qquad (12)$$

A plot of θ against lnC gives a straight line as indicated in Fig. 7, if Temkin isotherm is follow.

El-Awady isotherm: This model is also referred to as the kinetic/thermodynamic model and is written as follows:

$$\log\left(\frac{\theta}{1-\theta}\right) = logk + ylog\ C \qquad (13)$$

where,

y = The number of inhibitor molecules occupying one active site of the metal surface
θ = The degree of surface coverage
C = The inhibitor concentration, ppm

A plot of log(θ/1-θ) against logC as shown in Fig. 8 can be used to determine the associated parameters such as the reciprocal of y which is used to describe the number of active sites on the surface occupied by one molecule of the inhibitor. It can be related to the binding constant, B, according to Eq. (14):

$$B = k^{1/y} \qquad (14)$$

When 1/y>1, each inhibitor molecule is believed to occupying more than one active site on the metal surface and vice-versa (Fouda and Ellithy, 2009).

Based on Table 4 to 7, the R^2 values obtained from the linear regression of the experimental data showed they are close to unity which revealed that the adsorption of Okro leaf extract molecules onto the surface of carbon steel is strongly fitted to Langmuir, Temkin and Freundlich isotherms. Though, the Langmuir plot is linear with good correlation coefficient values, the slopes are greater than 1 this indicates a variation from an ideal Langmuir adsorption equation (Alhaffar *et al*., 2018; Solomon *et al*., 2010). It can be inferred that there is an interaction between surface of carbon steel metal and species of adsorbed inhibitor molecules. The value of intensity of adsorption shown in Table 5 from Freundlich isotherm is less than unity which specify that the adsorption is moderate. The adsorption capacity (K_{ads}) of the inhibitor decreased as temperature is increased which shows the reaction is exothermic in nature.

Table 6 gives the Temkin isotherm model parameters where the effect of indirect adsorbate

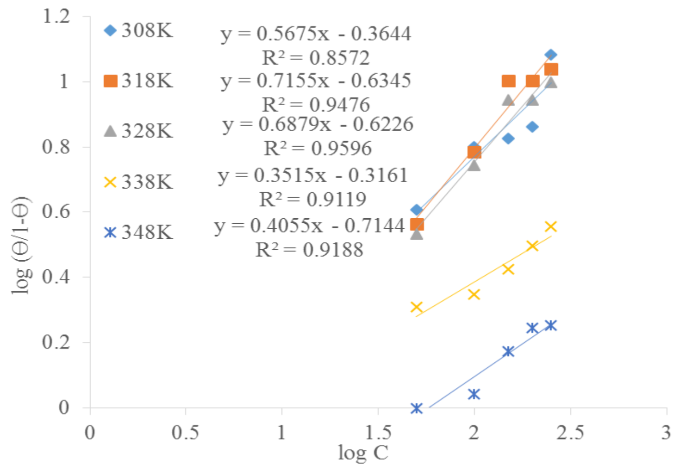

Fig. 8: El-Awady isotherm for adsorption of inhibitor on carbon steel surface

Table 4: Langmuir adsorption isotherms parameters

Temperature, (K)	K_{ads}	R^2	ΔG (KJ/mol)
308	0.088	0.998	-4.061
318	0.091	0.9997	-4.281
328	0.084	0.9997	-4.198
338	0.053	0.9978	-3.01
348	0.026	0.9949	-1.061

Table 5: Freundlich adsorption isotherm parameters

Temperature, (K)	K_{ads}	R^2	n	ΔG (KJ/mol)
308	0.647	0.8867	0.0612	-9.17
318	0.546	0.9065	0.0962	-9.02
328	0.508	0.9646	0.1096	-9.11
338	0.453	0.967	0.0967	-9.06
348	0.241	0.9314	0.1799	-7.50

Table 6: Temkin adsorption isotherm parameters

Temperature, (K)	K_{ads}	R^2	f	ΔG (KJ/mol)
308	4,448.5	0.9133	15.29	-31.79
318	257.89	0.9308	11.90	-25.29
328	164.54	0.9456	11.53	-24.87
338	253.22	0.9278	14.33	-26.84
348	2.76	0.9193	10.13	-14.55

Table 7: El-Awady adsorption isotherm parameters

Temperature, (K)	K_{ads}	R^2	y	1/y	B	ΔG (KJ/mol)
308	0.4321	0.8572	0.5675	1.762	0.23	-8.140
318	0.232	0.9476	0.7155	1.398	0.129	-6.76
328	0.238	0.9596	0.6879	1.454	0.124	-7.04
338	0.483	0.9119	0.3515	2.845	0.126	-9.24
348	0.393	0.9188	0.4055	2.466	0.099	-8.92

(inhibitor)/adsorbate (inhibitor) interactions with the metal surface on the adsorption process was confirmed. Generally, the coefficient of inhomogeneity (f) decreases except at 338 K. The Gibb's free energy of adsorption (ΔG°_{ads}) values obtained pointed towards chemisorption which is nature of Temkin isotherm. It means that there is a charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (Popova *et al*., 2003).

From Table 7, the value of 1/y obtained for the inhibitor is >1 which showed each molecule of the inhibitor is believed to occupy more than one active site on the carbon steel metal surface (Fouda and Ellithy, 2009). Similar results on value of y were reported by Umoren *et al*. (2008) and Umoren *et al*. (2009). The K_{ads} obtained in this study decreased with increase in temperature, indicating possible decrease in the rate of Okro leaf extract molecules condensation on the carbon steel surface probably due to high temperature which brought desorption corroborating (Ituen *et al*., 2017). As indicated in Table 7, the binding constant (B) decreases as temperature increases which shows that the interaction of inhibitor molecules on the metal surface decrease as a result of co-ordinate bond. The calculated values of ΔG°_{ads} listed in Table 4, 5 and 7 are in the range -1.061-9.24 kJ/mol these values indicates

Table 8: Experimental data for observed, predicted and residual on corrosion process

Run order	X_1, (ppm)	X_2, (Hr)	X_3, (°C)	Actual value	Predicted values	Residual
1	-1	+1	0	0.638	0.64	-0.00475
2	0	+1	-1	0.22	0.21	0.014
3	0	0	0	0.244	0.24	0.0018
4	0	0	0	0.243	0.24	0.0008
5	+1	+1	0	0.399	0.4	0.002
6	0	0	0	0.241	0.24	-0.0012
7	+1	-1	0	0.084	0.079	0.00475
8	0	+1	+1	0.882	0.89	-0.011
9	0	-1	0	0.054	0.043	0.011
10	0	-1	+1	0.204	0.22	-0.014
11	-1	-1	0	0.12	0.12	-0.002
12	+1	0	0	0.084	0.1	-0.016
13	+1	0	+1	0.459	0.45	0.008875
14	-1	0	+1	0.69	0.67	0.016
15	0	0	0	0.241	0.24	-0.0012
16	0	0	0	0.242	0.24	-0.0002
17	-1	0	-1	0.155	0.16	-0.008875

Table 9: Analysis of variance (ANOVA) of regression equation

Sources	Sum of squares	Df	Mean square	F-values	Prob>F, p-value
RSM model	0.88	9	0.098	519.78	<0.0001 Significant
Residual	0.001314	7	0.0001876		
Lack of fit	0.001307	3	0.0004356	256.23	<0.0001 Significant
Pure error	0.0000068	4	0.0000017		
Cor total	0.88	16			
R-squared	0.9985				
Predicted R-squared	0.9762				
Adjusted R-squared	0.9966				
Adequate precision	80.880				

spontaneous adsorption of inhibitor molecules on the metal surface. These values are less negative than -20 kJ/mol, from literature value of $\Delta G°_{ads}$ = -20 kJ/mol or less shows physisorption that involved electrostatic interaction between charged molecules whereas those in the order of -21 to -40 kJ/mol or more is taken as chemisorption that involved transfer or sharing of charge from the inhibitor to the surface of metal to form a kind of co-ordinate bond (Yaro and Khadom, 2008; Roy *et al*., 2014).

From the values of $\Delta G°_{ads}$ obtained in this study, it can be suggested that mechanisms of adsorption of Okro leaf extract on carbon steel surface might involve two types of interface namely physisorption and chemisorption. It can be said that adsorption occurred first on the metal surface due to physisorption as a result of effective adsorption of molecules of water on the surface of carbon steel. The unused part of the water molecules adsorbed on the metal surface is complemented by a chemical interaction between the metal surface and the inhibitor that showed chemisorption adsorption process.

Optimization of corrosion process on carbon steel: Table 8 shows the experimental data for the predicted, observed and residual values obtained, the small values of the residual indicate that the data from the experiment fitted well to the quadratic model used. Also, results of the Analysis of Variance (ANOVA) as presented in Table 9 showed the model used was significant with F-value of 519.78 and with a corresponding low p-value ($p<0.00010$).

For the model to be adjudged to be of good fit R^2 value should be at least 0.80 (Guan and Yao, 2008). The coefficient of determination (R^2) value of 0.9985 (Fig. 9) gotten showed the good fit of the model which indicates the sample variation of 99.85% dependent variable was ascribed to the independent factors and also it can be seen that only 015% of the total variation could not be elucidated by the model. Figure 10 give the normal plot of residual that shows little deviations from the normal revealing the good fit of the model. The larger value of lack of fit indicate the model is significant. Therefore, it can be suggested that the model obtained could be used in theoretical prediction of the dependent variable (Betiku and Adesina, 2013). Table 10 depicts the result of test of significance for all the coefficient of regression. It showed that the p-values of the model terms X_1, X_2, X_3, X_1X_2, X_1X_3, X_2X_3, X_1^2, X_2^2 and X_3^2 were significant at 5% confidence level ($p<0.5$). The model equation in terms of coded factors for the prediction of weight loss of carbon steel is expressed in Eq. (15) Table 11:

$$\text{Weight loss} = 0.24 - 0.072\ X_1 + 0.21\ X_2 + 0.22\ X_3 - 0.051\ X_1X_2, - 0.040\ X_1X_3 + 0.13\ X_2X_3 + 0.038\ X_1^2 + 0.031\ X_2^2 + 0.067\ X_3^2 \quad (15)$$

Figure 11 to 13 describes the surface plot for the weight loss of carbon steel corrosion process using Okro leaf extract as inhibitor. It was used to give an important evidence on the system behaviour within the experimental design on the corrosion of carbon steel using Okro leaf as an inhibitor. The different shapes of

Table 10: Test of significance for coefficient of regression

Sources	Sum of squares	Df	Mean square	F-values	Prob>F, p-value
X_1	0.042	1	0.042	221.78	<0.0001
X_2	0.35	1	0.35	1873.39	<0.0001
X_3	0.37	1	0.37	1975.28	<0.0001
X_1X_2	0.01	1	0.01	54.90	0.0001
X_1X_3	0.0064	1	0.0064	34.11	0.0006
X_2X_3	0.066	1	0.066	349.25	<0.0001
X_1^2	0.005929	1	0.005929	31.60	0.0008
X_2^2	0.0003923	1	0.003923	20.91	0.0026
X_3^2	0.019	1	0.019	101.55	<0.0001

Table 11: Optimization objective

Constraints	Goal	Lower limit	Upper limit
Concentration of inhibitor	In range	50	250
Contact time	In range	2	12
Temperature	In range	35	55

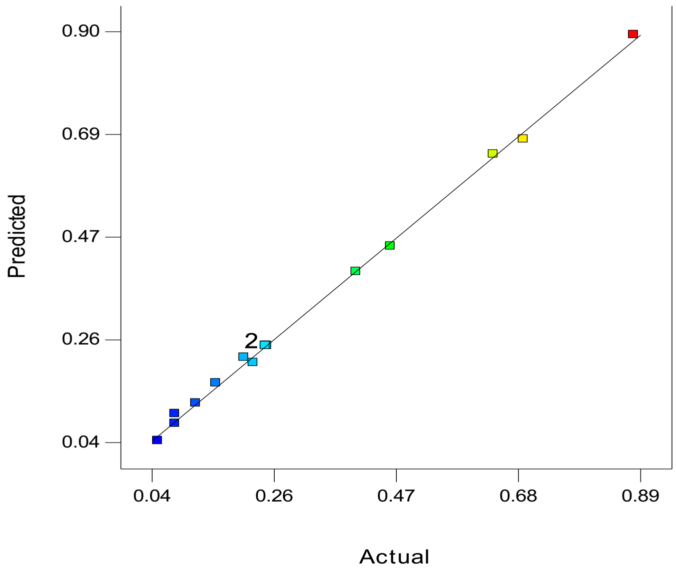

Fig. 9: Plot of experimental and predicted

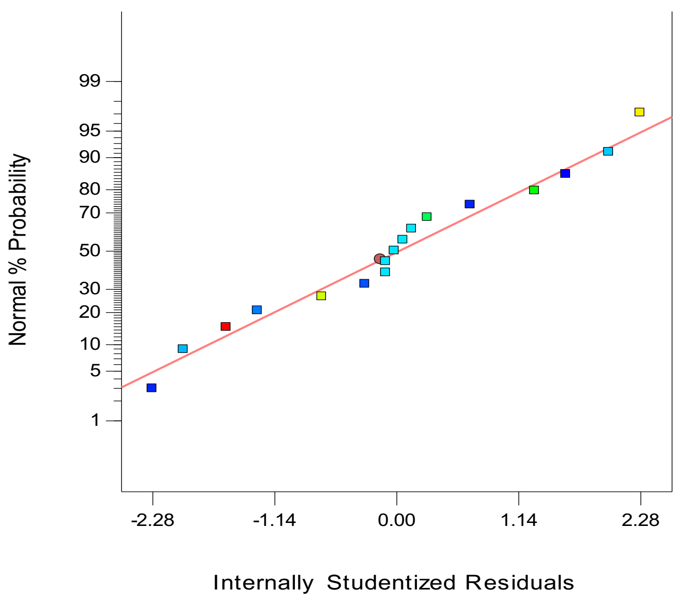

Fig. 10: Normal plot for the residual

the contour plots indicated different interactions between the variables. An elliptical contour plot indicated interactions between the variables were significant while a circular contour plot means otherwise (Zhao *et al*., 2012). It can be seen in Fig. 11 that as concentration increases with contact time the weight loss of carbon steel decreases.

This can be as a result of higher adsorption of active inhibitor molecules from the extract on the metal surface forming a thin film on the metal surface thus preventing further attack from the corrosive environment. This in turn reduced the weight loss by specimen, which agrees with the findings of Yawas (2005) and Nwabanne and Okafor (2011). Figure 12 shows the interaction of concentration, temperature and weight loss. It can be deduced that the protective films of the inhibitor formed on the surface of the carbon steel are less stable at higher temperature thus leading to reduced weight loss at higher temperature. This may be due to desorption of some adsorbed molecules from the carbon steel surface at higher temperature thereby making the greater area of carbon steel to be exposed to attack from the acidic environment. Figure 13 revealed that at lower temperature and contact time, the weight loss of the carbon steel reduces. The Optimization tool of Design Expert 7.00 was used for the optimization. The goal of the optimization is to minimize the weight loss of carbon steel using the constraints shown in Table 11. The predicted optimal condition was; 198.71 ppm 2.04 h and 40.29°C for the concentration of inhibitor, contact time, temperature respectively while 0.045 g was the least weight loss predicted. The predicted optimum condition of the model was validated by conducting three replicates of experiments in the laboratory, 0.051 g weight loss of carbon steel was obtained which is in the range of the predicted value by the model equation.

CONCLUSION

In the present study, Okro leaf was extracted and characterized using phytochemical test and was used as an inhibitor. The effects of corrosion inhibition of the Okro leaf extract for carbon steel in 1.5M HCl solution

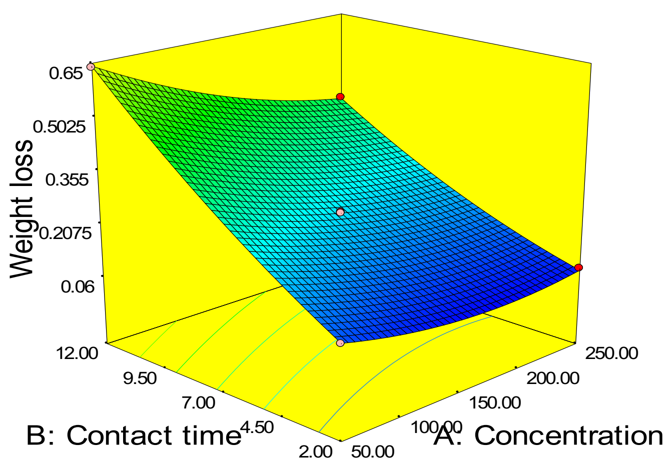

Fig. 11: Surface plot for the effect of contact time, inhibitor concentration on weight loss of carbon steel

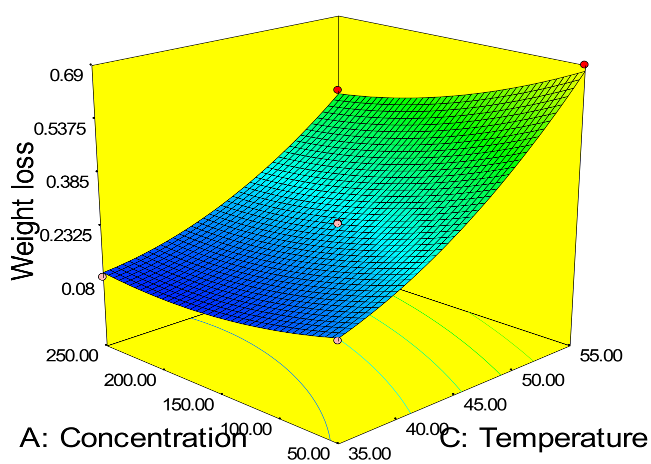

Fig. 12: Surface plot for the effect of temperature and inhibitor concentration on weight loss of carbon steel

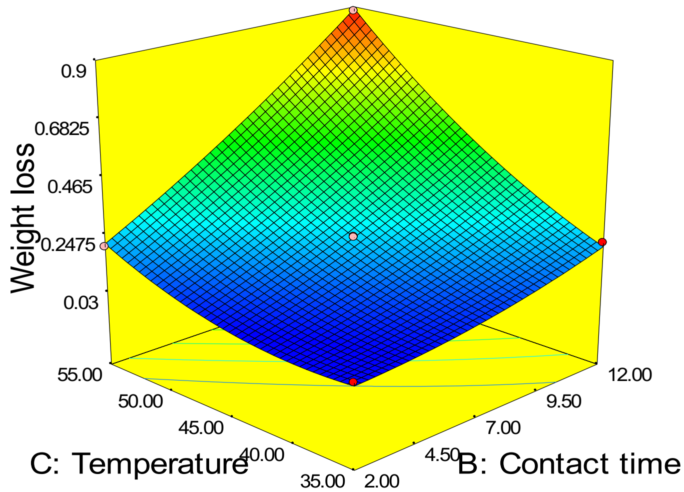

Fig. 13: Surface plot for the effect of temperature and contact time on weight loss of carbon steel

was estimated using the gravimetric technique. Thermodynamic, adsorption and optimization studies were also carried out to estimate the binding/adsorption mechanism of the inhibitor molecules on the surface of the carbon steel. The corrosion rate decreased as inhibitor concentration is increased. The corrosion inhibition performance of Okro leaf extract is found to depend on its concentration and temperature. Corrosion inhibition of the Okro leaf extract on carbon steel surface occurred by the physical adsorption mechanism. This was evidenced with the values of activation energy obtained in the inhibited medium which is higher than that obtained in the blank solution. In addition, the rate of corrosion was maximum in the blank solution since it is devoid of inhibitor that can impede the corrosion deterioration process. The effects of inhibitor concentration, contact time and temperature on weight loss of carbon steel is carried out using Response Surface Methodology (RSM). It was established that all the variables considered are significant factors on the corrosion inhibition process. Second-order mathematical model fitted well to the experimental data obtained. The optimum condition that was established were; 198.71 ppm 2.04 h and 40.29°C for the concentration of inhibitor, contact time, temperature respectively. The activation enthalpy of the corrosion process increases from 22.89 kJ/mol to 55.69 kJ/mol. The positive values of the enthalpy of the corrosion system signified an endothermic adsorption process. The activation entropy ($\Delta S°$) values in the absence and presence of inhibitor were all negatives. This implied to mean that the activated complex in the rate - determining step represents association rather than dissociation step, indicating that during the adsorption process, a decrease in the degree of orderliness takes place. Experimental data fitted well to Langmuir, Freundlich and El-Awady isotherms. However, mixed type adsorption mechanisms were confirmed on corrosion inhibition of Okro leaf extract on the carbon steel surface. The adsorption process is spontaneous with the negative value of $\Delta G°_{ads}$ obtained.

CONFLICTS OF INTEREST

This research article is an original work of the authors and was carried out by the authors. The authors declare no conflict of interest in whatsoever form.

REFERENCES

Abd El-hameed, R.S., 2011. Aminolysis of polyethylene terephthalate waste as corrosion inhibitor for carbon steel in HCL corrosive medium. Adv. Appl. Sci. Res., 2(3): 483-499.

Adepoju, T.F. and U.P. Eyibio, 2016. Study on oil extraction from Citrullus Lanatus (C. lanatus) oilseed and its statistical analysis: A case of Response Surface Methodology (RSM) and Artificial Neural Network (ANN). Chem. Res. J., 1: 28-36.

Alhaffar, M.T., S.A. Umoren, I.B. Obot and S.A. Ali, 2018. Isoxazolidine derivatives as corrosion inhibitors for low carbon steel in HCl solution: Experimental, theoretical and effect of KI studies. RSC Adv., 8: 1764-1777.

Betiku, E. and O.A. Adesina, 2013. Statistical approach to the optimization of citric acid production using filamentous fungus Aspergillus Niger grown on sweet potato starch hydrolyzate. Biomass Bioenerg., 55: 350-354.

Cheng, S., S. Chen, T. Liu, X. Chang and Y. Yin, 2007. Carboxymenthylchitosan as an ecofriendly inhibitor for mild steel in 1 M HCl. Mater. Lett., 61(14-15): 3276-3280.

Dheba, M.A., M.E. Salem and A. Khaled, 2017. Phytochemical screening of abelmoschus esculentus from Leptis area at Al-Khums Libya. Int. J. Chem. Sci., 1(2): 48-53.

El Maghraby, A.A., 2009. Corrosion inhibition of aluminum in hydrochloric acid solution using potassium iodate inhibitor. Open Corrosion J., 2(1): 189-196.

Fouda, A.S. and A.S. Ellithy, 2009. Inhibition effect of 4-phenylthiazole derivatives on corrosion of 304L stainless steel in HCl solution. Corrosion Sci., 51(4): 868-875.

Guan, X. and H. Yao, 2008. Optimization of viscozyme L-assisted extraction of oat bran protein using response surface methodology. Food Chem., 106(1): 345-351.

Hui, C., S. Wenyan, S. Jinling and X. Qi, 2012. Study of *Stevia Rebaudiana* leaves as green corrosion inhibitor for mild steel in sulphuric acid by electrochemical techniques. Int. J. Electrochem. Sci., 7(4): 3726-3736.

Ituen, E., O. Akaranta and A. James, 2017. Evaluation of performance of corrosion inhibitors using adsorption isotherm models: An overview. Chem. Sci. Int. J., 18(1): 1-34.

Njoku, E.R., 1998. Effect of Inhibitors on Corrosion of Mild Steel in HCL Pickling Solution. M.Sc. Thesis, Department of Metallurgical Engineering, ABU, Zaria Nigeria.

Nnanna, L.A., B.N. Onwuagba, I.M. Mejeha and K.B. Okeoma, 2010. Inhibition effects of some plant extracts on the acid corrosion of aluminium alloy. Afr. J. Pure Appl. Chem., 4(1): 011-016.

Nnanna, L.A., K.O. Uchendu, F.O. Nwosu, U. Ihekoronye and E.P. Eti, 2014. Gmelina Arborea Bark Extracts as a Corrosion Inhibitor for mild steel in an acidic environment. Int. J. Mater. Chem., 4(2): 34-39.

Norzila, M. and A.S. Ishak, 2015. Thermodynamic study of corrosion inhibition of mild steel in corrosive medium by piper nigrum extract. Indian J. Sci. Technol., 8(17): 1-6.

Nwabanne, J.T. and V.N. Okafor, 2011. Inhibition of the corrosion of mild steel in acidic medium by Vernonia Amygdalina: Adsorption and thermodynamics study. J. Emerg. Trends Eng. Appl. Sci., 2(4): 619-625.

Nwigbo, S.C., V.N. Okafor and A.O. Okewale, 2012. Comparative study of elaeis guiniensis exudates (Palm Wine) as a corrosion inhibitor for mild steel in acidic and basic solutions. Res. J. Appl. Sci. Eng. Technol., 4(9): 1035-1039.

Ogoke, E.C., S.A. Odoemelam, B.I. Ita and N.O. Eddy, 2009. Adsorption and inhibitive properties of clarithromycin for the corrosion of Zn in 0.01 to 0.05 M H_2SO_4. Port. Electrochim. Acta, 27(6): 713-724.

Oki, M., E. Charles, C. Alaka and T.K. Oki, 2011. Corrosion inhibition of mild steel in hydrochloric acid by tannins from Rhizophora Racemosa. Mater. Sci. Appl., 2(6): 592-595.

Omoruwou, F., A.O. Okewale and C.N. Owabor, 2017. Statistical analysis of corrosion inhibition of water hyacinth on mild steel in an acidic medium. J. Environ. Anal. Toxicol., 7(4): 1-5.

Owate, I.O., O.C. Nwadiuko, I.I. Dike, J.O. Isu and L.A. Nnanna, 2014. Inhibition of mild steel corrosion by aspilia Africana in Acidic Solution. Am. J. Mater. Sci., 4(3): 144-149.

Paul, O.A., M. Ladan and S. Takuma, 2012. Corrosion inhibition and adsorption behaviour for mild steel by ficus glumosa gum in H_2SO4 solution. Afr. J. Pure Appl. Chem., 6(7): 100-106.

Prithiba, A., S. Leelavathi and R. Rajalakshmi, 2014. Application of natural products as corrosion inhibitors in different steel and media. Chem. Sci. Rev. Lett., 3: 177-187.

Popova, A., E. Sokolova, S. Raicheva and M. Christov, 2003. AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives, Corrosion Sci., 45(01): 33-58.

Quraishi, M.A., A. Singh, V.K. Singh, D.K. Yadav and A.K. Singh, 2010. Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murraya koenigii* leaves. Mater. Chem. Phys., 122(1): 114-122.

Rajendran, S., R. Mari Joany, B.V. Apparao and N. Palaniswamy, 2000. Synergistic effect of calcium gluconate and Zn^2 on the inhibition of corrosion of mild steel in the neutral aqueous environment. Trans. SAEST, 35(3-4): 113.

Roy, P., A. Pal and D. Sukul, 2014. Origin of the Synergistic effect between polysaccharide and thiourea towards adsorption and corrosion inhibition for mild steel in sulphuric acid. RSC Adv., 4: 10607-10613.

Seramen, S., A. Rajendran and V. Thangavelu, 2010. Statistical optimization of anticholesterolemic drug lovastatin production by the red mold *Monascus purpureus*. Food Bioprod. Process., 88(2-3): 266-276.

Shivakumar, S.S. and K.N.S. Mohana, 2012. Ziziphus Mauritiana leaves extract as corrosion inhibitor for mild steel in sulphuric acid and hydrochloric acid solution. Eur. J. Chem., 3(4): 426-32.

Solomon, M.M., S.A. Umoren, I.I. Udousoro and A.P. Udoh, 2010. Inhibitive and adsorption behaviour of carboxymethyl cellulose on mild steel corrosion in sulphuric acid solution. Corrosion Sci., 52(4): 1317-1325.

Thirumoolan, D., V.A. Katkar, G. Gunasekaran, T. Kanai and K.A. Basha, 2014. Prog. Org. Coat., 77(2014): 1253-1263.

Umoren, S.A., I.B. Obot, E.E. Ebenso, P.C. Okafor, O. Ogbobe and E.E. Oguzie, 2006. Gum Arabic as a potential corrosion inhibitor for aluminium in alkaline medium and its adsorption characteristics. Anti-Corros. Method. M., 53(5): 277-282.

Umoren, S.A., I.B. Obot, E.E. Ebenso and P.C. Okafor, 2008. Eco-friendly inhibitors from naturally occurring exudate gums for Aluminium corrosion inhibition in acidic medium. Port. Electrochim. Acta, 26(3): 267-282.

Umoren, S.A., I.B. Obot, E.E. Ebenso and N.O. Obi-Egbedi, 2009. The inhibition of aluminium corrosion in hydrochloric acid solution by exudate gum from *Raphia hookeri*. Desalination, 247(1-3): 561-572.

Wang, M., J. Wang, J.X. Tan, J.F. Sun and J.L. Mou, 2011. Optimization of ethanol fermentation from sweet sorghum juice using response surface methodology. Energ. Source. Part A, 33(12): 1139-1146.

Yaro, A.S. and A.A. Khadom, 2008. Evaluation of the performance of some chemical inhibitors on corrosion inhibition of copper in acid media. J. Eng., 2(14): 2350-2362.

Yawas, D.S., 2005. Suitability assessment of some plant extracts and fatty acid vegetable oils as corrosion inhibitors. Ph.D. Thesis in the Department of Mechanical Engineering, ABU, Zaria-Nigeria.

Zhao, L.C., Y. He, X. Deng, G.L. Yaang, W. Li, J. Liang and Q.L. Tang, 2012. Response surface modeling and optimization of accelerated solvent extraction of four lignans from fructus schisandrae. Molecules, 17(4): 3618-3629.