Thermodynamic and Optimization Studies of Castor Leaf Extract as Corrosion Inhibitor on Stainless Steel (301)

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ABSTRACT: Inhibition of stainless steel corrosion in acidic medium with castor leaf extract was studied using the Gravimetric measurement. The mechanisms of inhibition, influence of temperature on inhibition efficiency and weight loss were determined for temperature range 40 ºC – 80 ºC at 7 hours immersion time. An increased in temperature showed a decreased in the inhibition efficiency of the castor leaf extract which resulted to increase in weight loss of the stainless steel. The value of rate constant for the corrosion process ranges from 0.333 – 1.225 hr^{-1}, this is seen to be directly relative to the inhibitor concentrations. Activation energy, enthalpy of activation, and entropy values ranges from 74.000 - 136.377 kJ/mol, 71.820 – 133.620 kJ/mol, and 9.860 – 178.110 J/molK respectively. Rise in activation energy with inhibitor concentration confirmed physisorption adsorption mechanism for stainless steel surface corrosion. In order to obtain the optimum weight loss, optimization of the process variables was carried out using the Box – Behnken Design plan and desirability function of response surface methodology (RSM). Four parameters were varied viz; time of immersion, HCl concentration, inhibitor's concentration, and temperature alongside their effects on weight loss of the stainless steel were verified. The optimal conditions predicted from the second order quadratic model were time (9.10 hours), HCl concentration (3.97 M), concentration of inhibitor (240.90 ppm), and temperature (78.67 ºC) with 2.978 g as the weight loss. Statistically, the results showed that 95.03% of the variation in total weight loss of stainless steel can be connected to the experimental variables examined.

KEYWORDS: Weight loss, activation parameters, adsorption, optimization, stainless steel, castor leaf

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I. INTRODUCTION

Nowadays the most vital consideration for industry is cutback of the complete cost by protection and conservation of resources used. The protection of metals from corrosion prevents waste of resources and money in industrial application and is vital to equipment lifespan, limiting the dissolution into the environment of toxic metals from the components (Kuye and Olanipekun, 2018). Metal loss by corrosion is a waste not only to the metal but also that of the human energy that is used in the construction and fabrication of the metal sheet in the first instance. The deterioration of the important properties of a metal material due to its reaction/interaction with the environment is called corrosion. Although many people believe that stainless steels are notable for their corrosion resistance as a result of their chromium content, but they do suffer from certain type of corrosion in some environment. In order to protect metals and their alloys from possible attack of corrosion, approaches such as; structure isolation from aggressive media using film-forming chemicals, or loss of electrons compensation (since corrosion is an oxidation process) and from the electrode configuration (e.g. cathodic protection by impressed current or by using active sacrificial anodes) (Omnia and Shehata, 2018).

In the midst of the numerous methods of preventing and controlling corrosion, the application of corrosion inhibitors, is becoming very common in combating corrosion in chemical process industries. Most of the proven inhibitors to be effective are; natural complexes which contain mostly atoms of nitrogen, sulphur, or oxygen in their compositions. The use of plant extracts as corrosion inhibitors have become significant because they are acceptable in the environment, not expensive, freely accessible, biologically acceptable, and sometimes constitute waste to the environment (Ambrish et al, 2012). Numerous findings has been carried out on use of natural products as corrosion inhibitors some of these are extracts from the leaves, flowers, seeds and roots that have been widely reported by several authors (Ekanem et al., 2010; Mourya et al., 2014; Okafor et al., 2008; Obot and Obi-Egbedi, 2009; Vimala et al., 2011; Uwah et al,, 2013; Oguzie et al., 2013; Ashassi Sorkhabi et al., 2015).

Optimization and statistical modeling is very essential in the design of experiment due to its enhancement of process efficiency deprived of an additional increase in the cost of process evaluation as well as process improvement. The one

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factor at a time (classical) method of carrying out experiment is very cumbersome, and utilize most of the time without even providing an effects of the variables/factors that is complete on the process. This do not give the mutual interactions effect among the physicochemical factors and can also lead to confusion in results interpretation (Bas and Boyaci, 2007). Collection of mathematical and statistical techniques that are very important in modeling and robust study of engineering problems whereby the response (yield) of interest is influenced by several variables is referred to as Response Surface Methodology (RSM) (Montgomery, 2001). The interactive influence of these process factors can be known through this method of experimental design. RSM is used for design of experiments, building numerical models, evaluating the effects of variables, and searching for maximum combinations of variables (Okewale et al., 2015).

II. MATERIALS AND METHODS

A. Materials

Castor leaves were procured from Akpugo community in Enugu State, Nigeria. Stainless steel was procured from accredited iron sheet dealer in Effurun, Delta State. It was machined in Mechanical Workshop at Federal University of Petroleum Resources, Effurun Delta State. Analytical grades (Sigma Alddrich) of HCl, acetone, and ethanol solutions were employed for the work.

B. Methods

1.) Sample characterization and pre-treatment

The Castor Leaf sample was thoroughly washed thereafter sun dried and pulverized into powdery form with the aid of laboratory blender. It was then sieved with a sieve of 0.143µm mesh. The sample was thereafter stored in a desiccator before use.

2). Extraction from Castor leave

40g of the dried castor leave powder was transferred into a 1000mL Soxhlet extractor. 500mL of 98% ethanol was reflux continuously for 3 hours at 78°C. The set-up was placed on a heating mantle and the castor leave extract was obtained by exhaustively heating the solution. The extract was obtained after ethanol was recovered in a Rotary evaporator (model R-210) at 40°C.

3.) Scanning Electron Microscopy Energy Dispersive X – rays Analysis

The elemental analysis of the stainless steel were performed at the Department of Chemical Engineering, Ahmadu Bello University, Zaria. The stainless steel was fixed on an appropriate metal stub and with adhesive on either side, and glazed with gold in a vacuum using a coater that is IB – 3ion using scan Phenom ProX (Eindhoven Netherlands), operating at 25Kv. The microscope was equipped with energy dispersive X- ray system with Prosuite elemental analysis software was used to obtain the distribution of element composition.

4.) Procedure of the experiment

The gravimetric method was used. The stainless steel was refined with an abrasive paper, degreased with ethanol, rinsed with distilled water and later dried in acetone. Each stainless steel coupon was sized 2cm × 4cm × 0.5cm. A hole of 0.1cm is bored on each metal coupon. The metal coupon was hovered into the 100ml beaker with 100ml of 1.5M hydrochloric acid at different inhibitor concentrations with the aid of thread. The various time intervals of 120, 240, 360, 480, 600 and 720 hours were used for the corrosion study at 30 ^{0}C.

The mechanism of inhibition and thermodynamic parameters were studied at 313, 323, 333, 343, and 353K temperature at contact time of 7 hours. The stainless steel coupon was subsequently immersed in distilled water and ethanol solutions. This was carried out so as to clean and eliminate any residual hydrochloric acid and castor leaf extract from the metal surface. The coupon was rinsed exhaustively with distilled water and washing liquor and subsequently dried in acetone before it is reweighed.

5.) Corrosion rate determination

The expression for measurement of corrosion rate (C.R) in millimeters penetration per year (mm/yr) as reported by (Callister, 1997) was used to measure the rate of corrosion rate for the specimens, as shown in eqn (1).

$$\text{C.R.} = \frac{87.6w}{at\rho} \quad (1)$$

where, w is corrosion weight loss of carbon steel (mg), a is the total surface area of the specimen in (cm^2), t is the exposure time in hours (hr), and ρ is the density of the specimen (g/cm^3).

6.) Determination of loss in weight

The loss in weight of stainless steel coupon was calculated using eqn (2).

$$Weight\ loss\ (g) = W - W_i \quad (2)$$

where, W is the initial weight of the stainless steel coupon, W_i is the weight of the stainless steel coupon after corrosion study.

7. Determination of castor leaf extract inhibition efficiency

The corrosion inhibition efficiency was determined using the eqn (3).

$$E(\%) = \frac{W_b - W_c}{W_b} \times 100 \quad (3)$$

where, W_b is the loss in weight in unconstrained solution (blank), and W_c is the loss in weight in constrained environment.

8.) Statistical analysis

8.1 Design of Experiment using Response Surface Methodology (RSM)

The design expert software (Design – Expert 7.00) was used for the experimental runs and modeling of experimental data. The process factors studied were immersion time (X_1), hydrochloric acid concentration (X_2), concentration of inhibitor (X_3), and temperature (X_4) alongside the factors levels is shown in Table 1. Twenty nine (29) runs of experiments were generated with BBD as depicted in Table 2.

Table 1: Variable levels of independent variables for Box-Behnken design.

Independent Value	Low level (-1)	Middle point (0)	High level (+1)
Exposure time, (hours)	2	7	12
Concentration of HCl, (M)	2	3	4
Inhibitor Concentration (ppm)	50	150	250
Temperature, (^oC)	40	60	80

Table 2 Box-Behnken Design of Experiment plan (Actual Value).

order	Immersion Time (hours)	Concentration of HCl, (M)	Inhibitor concentration (ppm)	Temperature, (^0C)
1	2	3	50	60
2	12	3	150	40
3	7	3	50	40
4	7	3	250	40
5	7	2	150	40
6	7	2	250	60
7	7	3	150	60
8	7	3	50	80
9	7	3	150	60
10	7	4	150	40
11	7	2	150	80
12	7	4	250	60
13	7	3	250	80
14	2	3	150	40
15	2	2	150	60
16	7	4	50	60
17	2	3	150	80
18	12	2	150	60
19	12	3	150	80
20	12	3	50	60
21	2	3	250	60
22	7	4	150	80
23	12	3	250	60
24	2	4	150	60
25	12	4	150	60
26	7	3	150	60
27	7	2	50	60
28	7	3	150	60
29	7	3	150	60

8.2 RSM regression model optimization

The quadratic model generated from the Response Surface Methodology is optimized with the aid of global surface response given by eqn (4).

$$Y=\beta_0+\sum_{i=1}^{k}\beta_i X_i+\sum_{i=1}^{k}\beta_{ii}X_i^2+\sum_{i<j}\beta_{ij}X_iX_j+e \qquad (4)$$

Y is the response (weight loss), i is the linear coefficient, the quadratic coefficients term is j, β is coefficient of regression while k is the factors studied, optimized in the experiment, and the random error is (e). For four parameters inputs x_1, x_2, x_3, and x_4 the equation of the quadratic response is given as eqn (5).

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 \qquad (5)$$

III. RESULTS AND DISCUSSION

A. Stainless steel Characterization

Table 3 shows result of the stainless steel ED-X analysis. It was seen that iron has the highest. As can be seen in Table 4 that castor leaf extract composed of saponin, reducing sugar, alkaloids, steroids, tannin, flavonoids, anthraquinones, terpenoids and carbohydrate while protein and phenolic compounds are absent in the extract. The occurrence of these constituents has been stated to encourage oxidation inhibition of stainless steel in aggressive acid media by adsorption on the surface of the metal (Umoren et al., 2006).

Table3: Result of the ED-X Analysis on stainless steel (301).

Elements	Weight Percentage (%)
Magnesium	0.47
Silicon	1.56
Bromine	2.24
Carbon	2.04
Oxygen	1.89
Molybdenum	1.38
Palladium	4.26
Iron	83.95
Nitrogen	0.2
Yttrium	1.12
Boron	0.88

Table 4: Result of the Phytochemical Analysis on castor leaf extract.

Constituents	Indication of Presence
Saponin	+
Reducing sugar	+
Alkaloids	+
Protein	-
Steroids	+
Tannin	+
Flavonoids	+
Anthraquinones	+
Phenolic compounds	-
Terpenoids	+
Carbohydrate	+

Key: present; -:Absent

B. *Influence of Temperature*

Figure 1 showed the influence of temperature on inhibition efficiency at 7 hours immersion time. The results revealed that the inhibition efficiency at different inhibitor concentrations decreased with a rise in acid medium temperature. A trend that signify physisorption mechanism. This can be due to the fact that the inhibitor protective film is formed on the surface of the stainless steel which is less stable at higher temperature. It can also be as a result of adsorbed molecules of inhibitor been desorbed from the metal surface at higher temperature thereby resulting to larger part of the stainless steel been exposed to attack from the acidic environment. The results achieved in this study is comparable to that described by Abd El-Hameed, (2011).

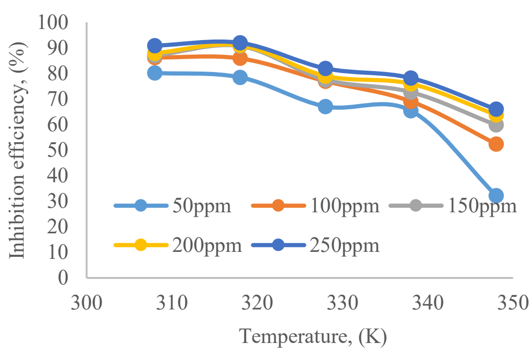

Figure 1: Effect of Temperature on corrosion inhibition efficiency.

C. *Kinetics Study*

1) First order plot

To obtain the half-life kinetics parameter, log (weight loss) against time of immersion was plotted and shown in Figure 2. The value of slope (k) obtained from the graph was used to calculate the half-life of the corrosion inhibition. As shown in Table 5, as the concentration of the inhibitor increases, the half-life of the inhibition process decreased. The correlation coefficient of determination (R^2) value obtained from the experimental data revealed that the data fitted well to the half –life kinetics model. The linear variation of Figure 2 also suggest pseudo-first order reaction kinetics on the metal surface oxidation in acidic solution, corroborating (Ijuo et al., 2016; Abeng et al., 2017).

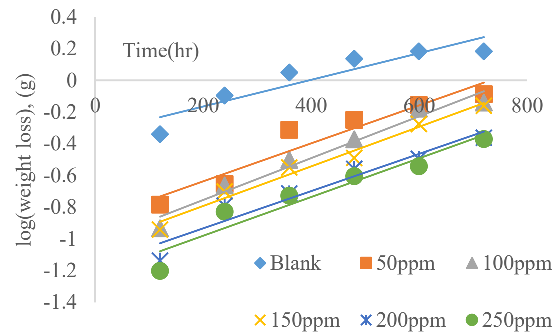

Figure 2: Kinetic plot of weight loss (g) against time (hr).

Table 5: Values of Half-life and R^2 values.

Inhibitor concentration, (ppm)	k	t, half-life (hr)
Blank	0.3325	2.084
50	0.8765	0.791
100	1.0185	0.680
150	1.0418	0.665
200	1.1664	0.594
250	1.2247	0.566

D. *Thermodynamic activation factors for the corrosion inhibition*

Arrhenius equation represented by eqn (6) was used to calculate the activation energy E_a in the presence and absence of castor leaf extract inhibitor.

$$\log C_R = \log A - \frac{E_a}{2.303RT} \quad (6)$$

where C_R is the corrosion rate, Ea is the apparent activation energy, R is the universal gas constant, T is the absolute temperature, and A is the frequency factor.

The Arrhenius plot of log C_R against reciprocal of absolute temperature (1/T) is shown in Figure 3 which showed a straight line graph with the gradient equal to -Ea/2.303R and the intercept equal to logarithm of pre-exponential factor (A). Hence, the apparent activation energy (Ea) and the pre-exponential factors (A) were calculated and tabulated in Table 6. These values of activation energy were found to range from 74.580 kJ/mol - 136.377 kJ/mol.

The value obtained for castor leaf inhibitor used was higher than that of the blank which indicates that the corrosion of stainless steel is retarded by the presence of castor leaf extract in HCl environment. It can also be observed that the activation energy value obtained is lesser in comparison to the ceiling limit value of 80 kJ/mol that is necessary for chemisorption adsorption mechanism in uninhibited solution (blank). The adsorption mechanism of castor leaf extract on metal surface was physisorption in nature in blank solution. Increase in Ea values indicates a very resilient inhibitive action of castor leaf inhibitor thereby increasing the energy barrier in the corrosion process which shows that the mechanism of the castor leaf extract adsorption on the surface of stainless steel is as a result of electrostatic interaction.

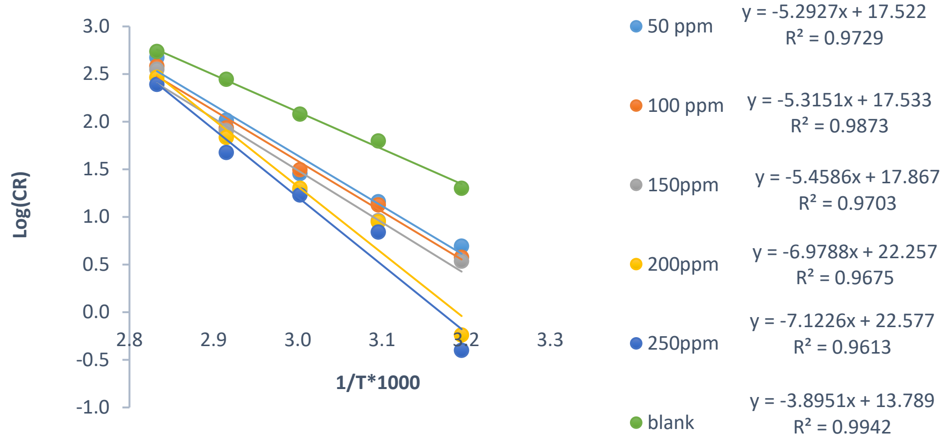

Figure 3: Arrhenius plot for corrosion inhibition of stainless steel.

This in not unconnected with the presence of organic molecules in the inhibitor that gets directly adsorbed on the metal surface by replacing protonated water, thereby forming protective film. Higher values of Ea greater than 80 kJ/mol in the presence of inhibitor is a good indication that the extract increases the energy barrier for the corrosion process which also confirms chemisorption in the inhibited medium. Increase in the activation energy can be attributed to substantial decrease in the adsorption of inhibitor on stainless steel surface as temperature rises because it is cathodic reaction that occurs in the corrosion cell which leads to hydrogen evolution in acidic medium studied. This process can also occurs because the castor leaf extract (inhibitor) forms an impassive film on the stainless steel metal surface, thereby making the iron (Fe) solubility in acidic medium to diminished. Similar results were reported in findings of (Eddy, 2009; Andreani et al., 2016).

Thermodynamic properties comprising of Enthalpy ($\Delta H°$) and Entropy of Activation ($\Delta S°$) are studied so as to ascertain the mechanism of adsorption the corrosion inhibition process was involved at the stainless steel surface. In other to compute the thermodynamic factors like (ΔH_{ads}), and entropy (ΔS_{ads}) of corrosion process in the presence and absence of castor leaf extract in hydrochloric acidic solution transition state theory equation represented by eqn (7) was used (Mouheddin et al., 2018;Ogoke et al., 2009).

$$log\left(\frac{C_R}{T}\right) = \left[log\left(\frac{R}{Nh}\right) + \frac{\Delta S^o}{2.303R}\right] - \frac{\Delta H^o}{2.303RT} \quad (7)$$

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 (8.314J/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 Figure 4 from which (ΔH^o) and (ΔS^o) values were inferred from the gradient and intercept of the graph correspondingly and shown in table 4. The enthalpy of activation (ΔH_{ads}) and the entropy of activation (ΔS_{ads}) were calculated, alongside their linear regression coefficient which is indicated in both figures 4 and table 6. The large positive values of ΔH_{ads} and ΔS_{ads} indicate that the adsorption of castor leaf extract on the surface of stainless steel is endothermic and spontaneous in nature respectively. The positive value of the entropy also signified that there is an increase in disorderliness of the inhibitor on the stainless steel surface. The energy of activation (Ea) values obtained were higher than the corresponding enthalpy of activation (ΔH_{ads}) which indicate that oxidation process might have indicate a reaction that is gaseous in nature, like the advancement of hydrogen reaction that is associated with decreasing the entire reaction volume.

Also, the mean difference between (Ea − ΔH_{ads}) value is 2.76 kJ/mol that is almost equal to the product of gas constant and temperature (RT) at a mean temperature of (333K) used. This result is in conformity with the perfect gas equation which suggest that the corrosion process is a unimolecular reaction (Elouali, et al., 2010). The results obtained showed the inhibitor performed evenly on activation energy (E_{ads}), and adsorption enthalpy (ΔH_{ads}). The result of this work is in agreement with the findings of (Larouj et al., 2017; Zarrouk et al., 2011). Large and positive values of entropies obtained showed that the activated complex in the rate determining step represents a dissociation rather than an association step, meaning that there is an increase in which the disordering takes place when going from reactants to the activated complex.

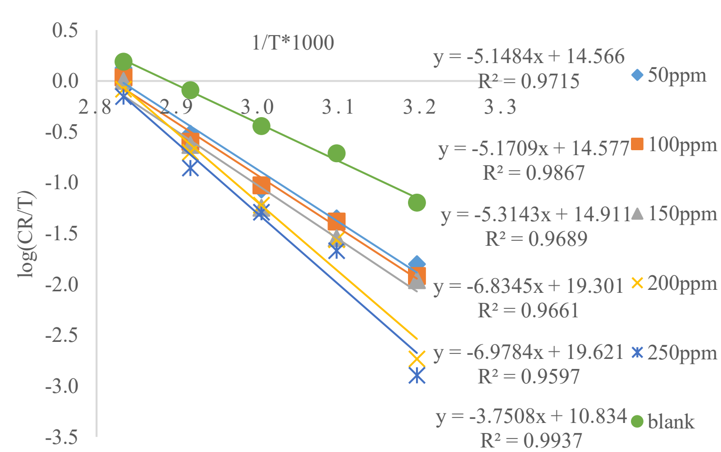

Table 6: Energy of Activation, entropy of activation, and enthalpy.

Inhibitor's Concentration (ppm)	Ea (kJ/mol)	ΔH^0 (kJ/mol)	A	Ea - ΔH^0	ΔS^0 (J/mol K)
Blank	74.58	71.82	6.15×10^{13}	2.76	9.86
50	101.34	98.58	3.30×10^{17}	2.76	81.32
100	101.769	99.00	3.41×10^{17}	2.76	81.53
150	104.517	101.75	7.36×10^{17}	2.76	87.93
200	133.624	130.88	1.81×10^{22}	2.74	171.98
250	136.377	133.62	3.78×10^{22}	2.76	178.11

E. *Statistical analysis of the Response Surface Methodology Quadratic Model of BBD*

Statistical testing of the quadratic model was done using analysis of variance (ANOVA) as shown in Table 7. The F – value was used to determine the significance of the model. The high Fisher's (F – value) of 19.12 and probability– value that is < 0.0001 obtained from the model equation for stainless steel weight loss as indicated in Table 7 showed that it was important. Experimental values achieved is fitted well to the second order quadratic model gotten.

The standard deviation value of 0.28 was achieved from the model. Coefficient of determination (R^2) value of 0.9503 was obtained for the model and this value is very closer to 1 which implied the projected value is near to the real value suggesting the value to be correct. The results from this work showed that the factors selected were adequately represented by the model. This also described that there is an actual correlation among the factors selected in the experiment. It showed that 95.03% of the total variation in the weight loss of castor leaf extract can be connected to the experimentally studied variables. The p – values was used to test the significance of each co-efficient in the model.

An adequate precision ratio of 17.058 was achieved in this investigation this suggest that the model can be used to navigate the design space and also an indication of adequate signal.

Adequate signal for the model obtained was confirmed with the value of precision ratio gotten. The goodness – of – fit of the regression equation was measured using the adjusted determination of coefficient (R^2). As seen in Table 8, adjusted R^2 value of 0.9006 was gotten from the model; this showed that the total variations not explained by the model were 9.94%. Predicted R^2 value of 0.7185 gotten was seen to be closer to the adjusted R^2.

The variation coefficient for the mean standard deviation with the data of experiment is 33.53%, this displayed an enhanced reliability and accuracy of the corrosion study as seen in Table 8 this also corroborate (Li et al., 2011; Rodrigues et al., 2012). The implication of each variable on corrosion process was established using both Probability and Fisher's values at 0.05 confidence level. It is seen that the oxidation of metal surface of stainless steel using castor leaf extract as inhibitor was significantly affected by (X1, X2, and X4 $p<0.0001$) linear terms. It is obvious that the interaction terms (X1X2, and X2X4) were significant at the level of $p<0.05$ and the quadratic terms (X22, and X42) were also significant at the level of $p<0.05$.

This elucidates an interface amid the studied process conditions that were noted as the core causes of weight loss alongside inhibition efficiency which in turn affect the corrosion rate of stainless steel. Response Surface Methodology model for the corrosion inhibition of stainless

Table 7 Analysis of variance Results for Quadratic Model of stainless steel weight loss.

Sources of data	Sum of the Squares	Degree of freedom	Mean Square	Fisher's – Values	Probability>F, P – Value
Model RSM	20.26	14	1.45	19.12	< 0.0001 significant
X_1	2.24	1	2.24	29.66	< 0.0001
X_2	5.45	1	5.45	72.07	< 0.0001
X_3	0.41	1	0.41	5.43	0.0353
X_4	9.22	1	9.22	121.86	< 0.0001
X_1X_2	0.97	1	0.97	12.82	0.0030
X_1X_3	0.093	1	0.093	1.23	0.2862
X_1X_4	0.081	1	0.081	1.07	0.3178
X_2X_3	0.23	1	0.23	3.04	0.1029
X_2X_4	0.77	1	0.77	10.23	0.0064
X_3X_4	0.005625	1	0.005625	0.074	0.7891
X_1^2	0.005487	1	0.00547	0.072	0.7917
X_2^2	0.39	1	0.39	5.21	0.0386
X_3^2	0.25	1	0.25	3.27	0.0921
X_4^2	0.37	1	0.37	4.95	0.0430
Residual	1.06	14	0.076		
Lack of fit	1.04	10	0.10	17.17	0.0073 significant
Pure error	0.024	4	0.006030		
Cor Total	21.32	28			

steel using castor leaf extract was optimized using the RSM function of desirability. As depicted in Table 9, it can be observed that the highest weight loss noted was 2.67 g but this value is small compared to the optimum weight loss obtained from the model as presented in Table 10. The maximum settings predicted from the quadratic second order polynomial equation were time (9.10 hr), concentration of HCl (3.97 M), concentratrion of inhibitor (240 ppm), and temperature (78.67 ºC) corresponding to the maximum weight loss of 2.978 g as shown in Table 10.

These values were validated with an average maximum weight loss of 3.03 g obtained after reproducing the experiments thrice and this was in conformity to the predicted maximum result of the RSM equation.

$$Y=5.48225-0.26504X_1-2.45483X_2+0.00275X_3-0.10143X_4+0.098500X_1X_2+0.022X_2X_4+0.24658X_2^2+0.000600833X_4^2 \quad (8)$$

Table 8: BBD Statistical Estimates.

Statistical estimates	
S. D.	0.28
Mean	0.82
Coefficient of Variation (%)	33.53
R^2	0.9503
R^2, Predicted	0.7185
R^2, Adjusted	0.9006
Precision of adequacy	17.058

F. *Plots of Surface Response*

3-D surface response plots generated from the model were presented in Figures (5 – 10) based on the analysis of the full quadratic model. This was used to provide a vital information surrounded by experimental design on the corrosion of stainless steel. Weight loss decreased with inhibitor concentration but it increases with rise in temperature

Table 9 Result obtained from the Box-Behnken Design of Experiment plan (Actual Value).

Std	Run order	Immersion Time (hours)	Concentration of HCl, (M)	Inhibitor concentration (ppm)	Temperature, (^{0}C)	Weight loss, (g)
17	1	2	3	50	60	0.17
10	2	12	3	150	40	0.06
5	3	7	3	50	40	0.04
6	4	7	3	250	40	0.03
21	5	7	2	150	40	0.02
15	6	7	2	250	60	0.13
28	7	7	3	150	60	0.58
7	8	7	3	50	80	2.09
26	9	7	3	150	60	0.46
22	10	7	4	150	40	0.12
23	11	7	2	150	80	0.80
16	12	7	4	250	60	1.30
8	13	7	3	250	80	1.93
9	14	2	3	150	40	0.01
1	15	2	2	150	60	0.04
14	16	7	4	50	60	2.39
11	17	2	3	150	80	1.35
2	18	12	2	150	60	0.27
12	19	12	3	150	80	1.97
18	20	12	3	50	60	1.52
19	21	2	3	250	60	0.06
24	22	7	4	150	80	2.66
20	23	12	3	250	60	0.80
3	24	2	4	150	60	0.47
4	25	12	4	150	60	2.67
25	26	7	3	150	60	0.61
13	27	7	2	50	60	0.26
29	28	7	3	150	60	0.55
27	29	7	3	150	60	0.43

Table 10: Result of the model optimization.

	X_1 Time, (Hr)	X_2 Concentration of HCl, (M)	X_3 Concentration of inhibitor, (ppm)	Temperature, (ºC)	Y, Weight loss (g)
Actual Variables	9.10	3.97	240.90	78.67	2.978

as depicted in Figure 5. This is as a result of additional castor leaf extract concentation present on the external area of the stainless steel that will be covered will be large thus inhibiting further corrosion on the metal surface. as inhibitincreasing time of exposure may quicken the degradation of the bioactive chemical compound in the inhibitor, which lead to lower inhibition effeiciency. Figure 6 showed the influence of hydrochloric acid concentration (x_2), temperature (x_4) towards weight loss, it can be observed that minimum weight loss was recorded at lower temperature with lower HCl concentration. Figure 6 also showed that the weight loss increased as the strength of acid increases. This is due to the fact that the amounts of hydrogen ions which are the active species are increased as acid concentration is increased (Fontana and Green, 1978).

This also affirmed the significant effect and positive synergy of the HCl concentration and temperature on the weight loss of stainless steel . Figure 7 depicted the outcome of concentration of hydrochloric acid (x_2), inhibitor concentration (x_3), on the weight loss on stainless steel, it was observed that lower inhibitor concentration favours higher weight loss but the weight loss decrease at lower HCl concentration towards the oxidation of the steel surface. It also inveterate the negative synergetic effect of these two terms on the stainless steel metal as shown in eqn (6). The influence of time (x_1), and temperature (x_4) upon the weight loss on stainless steel is shown in Figure 8.

It is shown that the weight loss increases as both time of immersion and temperature increases. This is due to the fact that cathodic reaction for stainless steel in acidic environment is governed by hydrogen evolution but on the reverse side, anodic reaction utilizes electrons produced at the cathode that leads to dissolution of iron. Meanwhile, the disappearance of the metal used was owing to increase in iron corrosion with increase in immersion time because of the incessant strike of hydrochloric acid towards the stainless steel that did not allow oxide to form upon the metal surface that can decrease the loss in weight. It can be assumed that as time is increase the weight loss of metal external surface was as a result of transfer of charges from inhibitor to the solution.

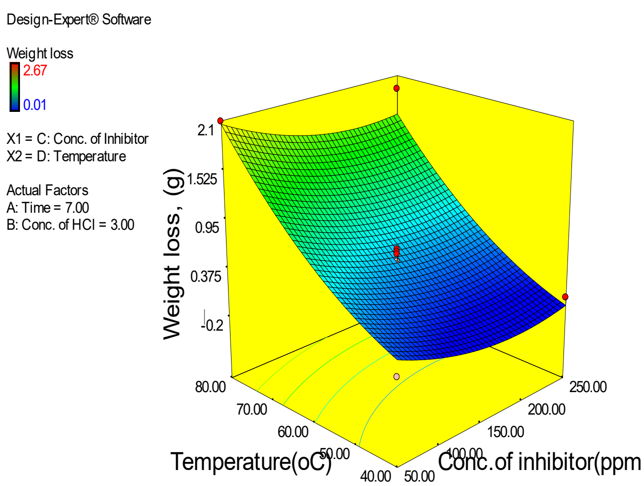

Figure 5: Effect of inhibitor's concentration, temperature, and boundary by weight loss.

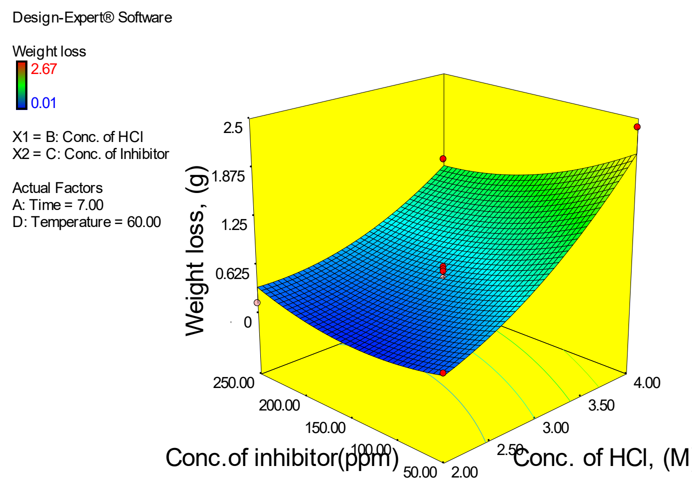

Figure 7: The effect of HCl concentration, inhibitor concentration, and boundary by weight loss plot.

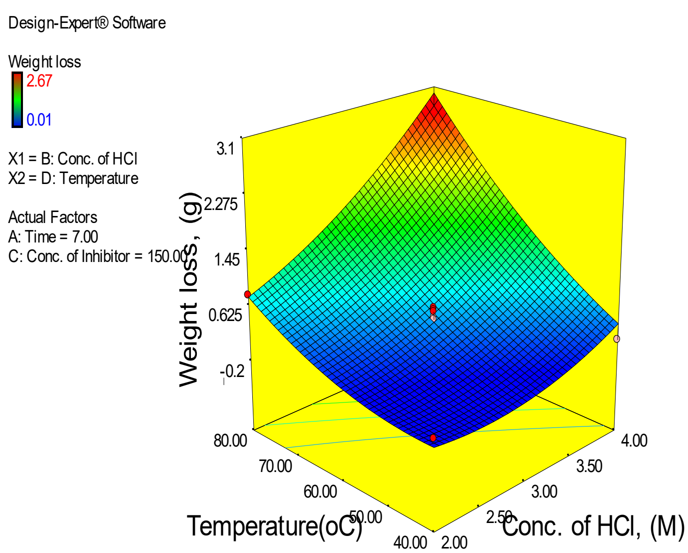

Figure 6: Effect of HCl concentration, temperature, and boundary by weight loss plot.

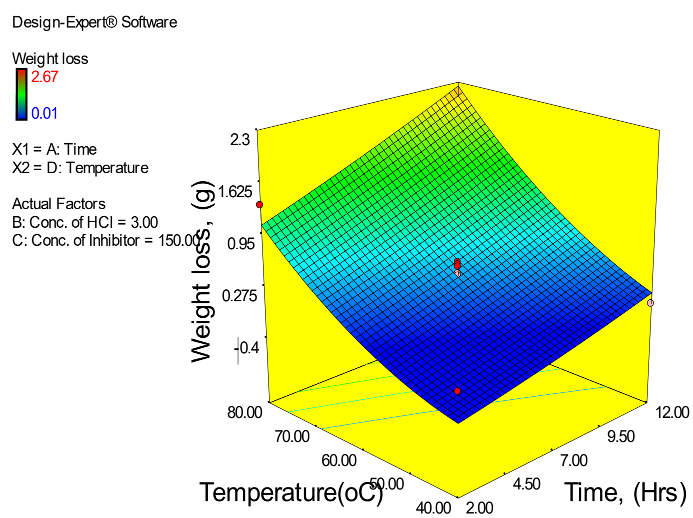

Figure 8: The effect of temperature, time and boundary by weight loss plot.

Figure 9 showed the influence of time (x_1), in addition with inhibitor concentration (x_3) on stainless steel loss in weight. It was revealed that there was a decrease in weight loss as concentration of inhibitor increases as a result of greater number of adsorption sites that are generated by numerous macromolecule concentrations of the castor leaf inhibitor upon the external steel surface. However, the loss of weight in stainless steel was seen to decreased with time which is attributed to the desorption of castor leaf inhibitor from the stainless steel surface. Figure 10 is an indication of the effect of time (x_1), and HCl concentration (x_2) on weight loss of stainless steel. It is evideent that as HCl concentration is increased with time the weight loss also increases due to the fact that chemical reaction rate increase as concentration of reactant is increase.

IV. CONCLUSION

The presence of Tannins, Saponins, flavonoids and other phytochemicals in the phytochemical analysis of the castor leaf extract suggest it to be a good corrosion inhibitor on stainless steel, as weight loss decrease with the addition of inhibitor. The kinetics and thermodynamic studies of the corrosion process shows the mechanism of adsorption of the inhibitor's molecule onto the surface of stainless steel. Activation energy values obtained for inhibited solution suggest chemisorption from the solution kinetics while physisorption is noticed in uninhibited solution. Both enthalpy and entropy of activation values were positive, this shows endothermic nature and associated mechanism of the inhibitor on the metal surface.

The coefficient of determination (R^2) value of 0.9503 was obtained, this inferred that the predicted data from the quadratic model fitted well with the actual data used. The predicted optimal terms using the second order quadratic model developed were time (9.10 hours), HCl concentration (3.97 M), concentration of inhibitor (240.90 ppm), and temperature (78.67 ^{o}C) with 2.978 g as the weight loss. These results predicted from the model were validated in three replicates and found to be in agreement with that of the experiment.

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