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RESEARCH PAPER

OPTIMIZATION AND STATISTICAL ESTIMATES OF LOCUST BEAN POD EXTRACT AS AN INHIBITOR TO COMBAT CORROSION ON ALUMINIUM METAL (AA3003) IN HYDROCHLORIC ACID

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ABSTRACT

To study the process of aluminium metal corrosion using locust bean pod as an inhibitor with a view to evaluating the weight loss, rate of corrosion, statistical data, and optimum process conditions in an aggressive medium was carried out using the gravimetry method. Optimization of the variables that affect corrosion of metals surface was undertaken with the aid of desirability function of the quadratic model in Response Surface Methodology (RSM). To obtain the maximum loss in weight of the aluminium metal in the presence of the locust bean pod inhibitor, four parameters were varied via; process time, the concentration of hydrochloric acid, locust bean pod extract concentration, temperature and their reciprocal effects on loss in weight aluminium metal were confirmed. The model predicted the optimum aluminium weight loss of 1.08187 g at 6.95 hours, 1.50 M, 111.98 ppm, and 64.12 ^{o}C for process time, hydrochloric acid concentration, locust bean pod extract concentration, and temperature, respectively. The existence of aromatic combination, and amine bond groups that are evidenced in locust bean pod FTIR analysis meet the descriptive qualities of typical corrosion inhibitors. An increase in HCl concentration led to an increase in the rate of aluminium metal dissolution in the inhibited and uninhibited media. The highest corrosion rate values obtained were 105.50 mm/yr and 103.35 mm/yr for uninhibited and 20 ppm inhibitor concentration respectively at 1.5 M HCl concentration. The useability of locust bean pod extract as an inhibitor in mitigating corrosion of aluminium metal in oil and gas facilities in the presence of hydrochloric acid and its optimum process values were confirmed in this present study.

Keywords: Weight loss, Central Composite Design, Modeling, Aluminium

IINTRODUCTION

Corrosion is one of the major setbacks in several technical installations or industries involving metals and alloys. Hence, prevention mechanism for the corrosion of metals is of utmost importance, to increase their lifespan, especially those in aggressive environments. Corrosion/or oxidation is the deterioration of metals in chemicals or reaction with its environment. Either type or nature of metal and the conditions of the environment in particular gasses which are in contact with the metal, determine the form of corrosion and the rate of its deterioration (Eugene Uwiringiyimana et al., 2016). Engineering corrosion is the discipline that is devoted to preventing, controlling, abating, and combating metal deterioration in process industry. In many frequent cases, corrosion can mean the electrochemical corrosion of iron in reaction with oxygen or sulphate as an oxidant. Rust also thrives in materials apart from iron, for instance ceramic/ polymer though, in this perspective, it is commonly known as material degradation. Corrosion vitiates the valuable material and structure properties, including appearance, strength, and perviousness to liquid, alloy oxidize simply by contacting the moist atmosphere, however, the technique can be fiercely influenced by contact with certain materials. Though, some oxidation mechanism is more noticeable and obvious. The chemistry of corrosion assists to comprehend the significance of metal surface oxidation. In – all purpose, iron materials develop an affinity to lose electrons and change into metal cations through metal oxidation. For aluminium reduction and oxidation reaction, the standard electrode potential indicates that it is a thermodynamically reactive metal, second only to magnesium among the common engineering metals (Revie and Uhlig 2008).

The mechanism of aluminium metal corrosion in a chloride solution such as HCl is very common in pitting corrosion. It is the most dangerous type of aluminium corrosion because it occurs as holes and pits of irregular shapes on the surface of the metal. The diameter and depth of the pits are dependent on the type of aluminium material, the corrosive medium, and the nature of the environment in which the exposure of the aluminium metal surface is made. Chloride ions attack the natural oxide layer, damaging it in the weakest parts, two main reactions occurred at the anodic sites, which are represented as equations 1 and 2 (Revie, 2011).

$$Al \leftrightarrow Al3+ + 3e- \quad (1)$$

$$Al3+ + 3H2O \leftrightarrow Al\ (OH)3 + 3H+ \quad (2)$$

Equation (2) shows that at anodic sites, a more acidic (pH = 3-4) environment is created. The chloride ions facilitate the anodic dissolution of aluminium, forming aluminium chloride (Revie, 2011). This hydrolyzes to form the hydroxide and acid, which shifts the pH to acidic values. Equations 3 – 5 show the cathodic sites' possible reactions on aluminium metals (Revie, 2011):

$$AlCl3 + 3H2O \leftrightarrow Al\ (OH)3 + 3HCl \quad (3)$$

$$3H+ +3e- \leftrightarrow H2 \quad (4)$$

$$O2 + H2O + 2e- \leftrightarrow 2OH- \quad (5)$$

The local hydroxide formation makes the cathodic sites to be more alkaline in nature. Pitting corrosion of aluminium frequently takes place in aerated chloride solutions. The exceptional properties offered by aluminum and its compound make it one of the highly multipurpose, cost-effective, and pleasant metallic material with a broad variety of applications that ranges from soft, and highly ductile packaging foil to highly demanding engineering products. Aluminum and its alloys are only second to steels that is in use as structural metals in industries (Davis, 1999). The African locust bean plant is a dicotyledonous angiosperm belonging to the family *Fabaceae* (Bello et al., 2019). African locust bean is classified under spermatophytes which are referred to as plants that are vascular in nature (Sylla, et al., 2002; Fasogbon, et al., 2016; Teklehaimanot, 2014). The pods of the tree that is generally denoted as locust beans are normally pink when it begins fruiting and subsequently turns to dark brown in colour at the end of its maturity period. The tree is usually 30–40 centimetres long on average basis, with some reaching lengths of about 45 centimetres (Bello et al., 2019). Each pod can contain up to 30 valuable seeds (Sylla, et al., 2002; Fasogbon, et al., 2016; Teklehaimanot, 2014) and once these seeds are harvested, the pods are discarded as waste material thereby constituting nuisance and solid waste pollution to the environment, it can also leads to health challenges or source of epidemic to human beings living around such environment once it starts degrading.

The use of classical method of experiment relating a lone variable in modeling and optimization has turn out to be outdated and do not reveal any interface among other parameters or variables that is studied in a process. The Response Surface Methodology (RSM) is a means of optimization that is made up of experimental configuration, study and modeling via fitting of the experimental variables/factors to partial regression (Wang at al., 2011). RSM have been established that it has capability to combine numerous variables /factors at an interval of time and display its mutual collaboration on the process yield. This also decreases the number of experimental runs required to provide adequate knowledge for results that are statistically acceptable (Betiku and Adesina, 2013; Adesina *et al*., 2019). RSM has been applied and is still being applied to corrosion inhibition processes, but none have been stated on inhibition of aluminium metal oxidation using locust bean pod as an inhibitor. The process variables previously reported that influenced the oxidation of the inhibition process were considered and optimized in this work. In order to maximize the loss in weight of aluminium metal in hydrochloric acid concentrations; RSM was utilized using the Central Composite Design (CCD) to verify the influences of four variables (time of immersion, locust bean pod (inhibitor), temperature of inhibition, and hydrochloric acid concentration) and their reciprocal consequences on loss in weight of aluminium metal surface. Both weight loss and corrosion rate of aluminium metal in HCl concentrations were determined using the gravimetric method. The impact of this metal (aluminium) protection process in different areas of application in homes and industries have necessitated a very keen interest by researchers in proffering solution to this menace by the use of corrosion inhibitors such as locust bean pod, will be of utmost benefit to the industry and environment due to its cost effectiveness, availability and environmentally friendly nature. There is little or no reports in literature to the best of our understanding, on the deployment of locust beam pod as a corrosion inhibitor on aluminium metal in HCl solution. Consequently, ascertaining this work novelty centering on the capability of locus bean pod in corrosion inhibition of aluminium metal.

MATERIALS AND METHODS

Materials

Locust bean pods (*Parkia Biglobosa*) were obtained from Ogbomoso Community in Oyo State, Nigeria. Aluminium metals were acquired from certified iron sheet merchandize in Effurun community of Delta State, Nigeria. The aluminium metals were processed into standard coupons in a Workshop of the Department of Mechanical Engineering, College of Engineering and Technology, Delta State, Nigeria. Surface organisation of the coupons that was mechanically polished were done with the aid of sand papers, washed by ethanol, degreased using acetone and later dried at atmospheric temperature. JENWAY model meter (pH – 3510), vacuum drying oven (DZF 6021), digital weighing balance (JJ 224BC), and beakers, were utilized for this oxidation process study. Analytical grades (Sigma Aldrich) of hydrochloric acid, acetone, and ethanol solutions were used while deionized water was employed for sample preparation.

Methods

Sample Preparation and Characterization

Locust bean pod samples were exhaustively cleansed and thereafter sun dried and pulverized into powdered form through the aid of laboratory blender (Kenwood). This is sieved with a sieve aperture size that is 0.143 µm. The sample was thereafter kept in a desiccator before use.

Analysis of Fourier Transform Infrared (FTIR) Spectroscopy

Locust bean pod extract of 0.143 µm is spotted with Fourier Transform Infrared (Buck Scientific model 530) Spectroscopy that has a wavelength which ranges from 500 – 4000 cm^{-1}. Potassium bromate (KBr) was used as background material for the analysis.

Extraction of Locust Bean Pod as Inhibitor (*Parkia Biglobosa*)

The locust bean pods (*Parkia Biglobosa*) were washed thoroughly with running water to remove debris. 300g of the pulverized locust bean pod powder was macerated in 96 % ethanol at room temperature in preparation for extraction in 500 mL soxhlet extractor. 300 mL of 96 % ethanol was constantly reflux for 3 hours at 78 ^{o}C. Locust bean pod extract of 2 g was weighed and dissolved in different molar concentration of hydrochloric acid used for the corrosion study.

Technique of Experimentation

Gravimetry loss in weight method was employed for the study. Each aluminium steel coupon was sized 40 mm × 20 mm × 2 mm. Prior to polishing of the aluminium coupons, 0.1 cm hole was bored on each coupon. Each aluminium coupon was weighed initially prior to suspension in a 100 ml beaker containing 50 ml of 0.5 M, 1 M, and 1.5 M HCl solution at different inhibitor concentrations 20 ppm, 70 ppm, and 120 ppm while the exposure time considered are 2 hrs, 5 hrs, and 8 hrs with the aid of a nylon thread. The temperatures considered were 35 ^{o}C, 50 ^{o}C and 55 ^{o}C, after the procedure of oxidation the coupon is immersed in both purified water and solution of ethanol, the corroded coupon was brushed to strip off any residual locust bean pod concentration and HCl concentration. Subsequently, the coupon is rinsed thoroughly with washing liquor, washed with purified water and afterward dried in acetone before it is weighed again to get the new weight. The weight loss of aluminium coupon was now used as the response for second order quadratic model of the central composite design for RSM analysis. The actual variables for the experimental plan is shown in Table 1.

Table 1: Design of Experiment Actual variables

Independent Variables	Lower level (-1)	Middle point (0)	Higher level (+1)
Exposure time (hours)	2	5	8
Inhibitor concentration (ppm)	20	70	120
Temperature (^oC)	35	50	55
Hydrochloric acid concentration (M)	0.5	1.0	1.5

Determination of weight loss

The loss in weight of aluminium metal coupon is ascertained using equation 6;

$$\text{Loss in weight, (g)} = Wo - Wf \quad (6)$$

Where, W_o is the initial aluminium coupon weight, W_f is the final aluminium coupon weight after oxidation study.

Calculation of Rate of Corrosion

The rate of aluminium metal corrosion was determined using equation 7;

$$\text{corrosion rate(mmpy)} = \frac{\text{kW}}{\text{ATD}} \quad (7)$$

Where, k is a constant with value as 87.6 mmpy, W is the weight loss (mg), A is the cross sectional area (mm^2), T is the time (hrs), D is the density of aluminium metal (g/cm^3) (Nwigbo et al., 2012).

Determination of Aluminium Metal Composition

The elemental composition of the aluminium metal was investigated using a scanning electron microscope equipped with energy dispersive X – ray (SEM – EDX) PHENOMWORLD that is operated at 25 kV. The metal surface was fixed to a metal stubs with adhesive on either side, and glazed with gold in a vacuum using a coater that is IB – 3ion and allowed to pass through the dispersive X – rays of the SEM machine. This was carried out at the Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria.

Optimization studies of corrosion inhibition process on aluminium

Optimization of the process variables that influenced the rate of oxidation was conducted using the CCD of Response Surface Methodology (RSM). The RSM study will show the magnitude and quality of the effect of each parameter, which is used to forecast the combination of parameters in reducing the rate of corrosion (Femiana *et al*, 2018). The four factors varied were temperature, locust bean pod extract concentration, hydrochloric acid concentration, exposure time and their corresponding influences on loss in weight of aluminium metal corrosion in acidic medium was investigated. Twenty nine (29) runs of experiments were produced using Central Composite Design of experiment (CCD) as seen in Table 2. Evaluation of model fitness is done via the test of significance and analysis of variance (ANOVA). The chosen variables, exposure time, concentration of hydrochloric acid, locust bean pod extract concentration, and temperature that are represented as X_1, X_2, X_3 and X_4 respectively. Results were analyzed and modeled using Design Experts 7 software. The coefficient of the polynomial model was finalized with the aid of multiple regressions as shown in Equation (8).

$$Y = b_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j} \beta_{ij} X_i X_j + e \quad (8)$$

Where, Y is the response that is loss in weight of aluminium, b_o is the intercept, b_{ij} is the interaction effect, and b_{ii} denotes the quadratic coefficients of X_i, and e is the randomized error (Omoruwou *et al.*, 2017).

Table 2: Central Composite Design (CCD) of Experiment Plan for Actual Values

Run	X1: Time (Hrs)	X2: Conc. of HCl (M)	X3: Conc. of inhibitor (ppm)	X4:Temperature (ºC)
1	5.00	1.00	70	50
2	2.00	1.00	120	50
3	5.00	0.50	120	50
4	5.00	1.50	120	50
5	5.00	1.00	120	65
6	5.00	1.00	70	50
7	5.00	1.00	70	50
8	8.00	1.00	70	35
9	2.00	1.50	70	50
10	2.00	0.50	70	50
11	5.00	0.50	70	65
12	8.00	1.00	120	50
13	5.00	1.00	20	35
14	8.00	1.00	20	50
15	5.00	1.50	70	35
16	5.00	0.50	70	35
17	8.00	1.00	70	65
18	2.00	1.00	20	50
19	8.00	1.50	70	50
20	5.00	1.00	20	65
21	5.00	1.00	120	35
22	2.00	1.00	70	35
23	2.00	1.00	70	65
24	5.00	1.50	70	65
25	5.00	1.00	70	50
26	8.00	0.50	70	50
27	5.00	1.00	70	50
28	5.00	1.50	20	50
29	5.00	0.50	20	50

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

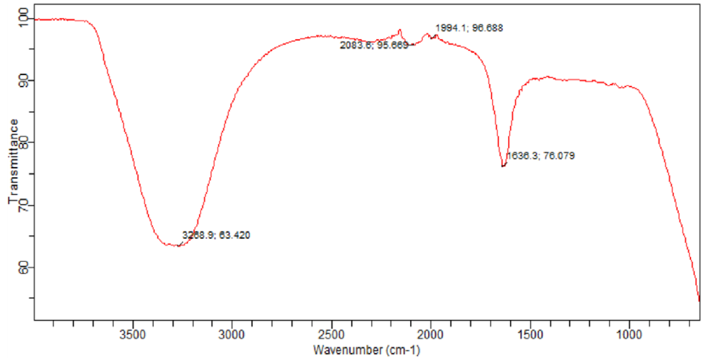

Figure 1 FTIR Spectra for locust bean pod extract

Figure 1 presents the FTIR spectra for the locust bean pod extract. It can be noted that frequency 1638.3 cm^{-1} is assigned to –C – O stretching of ketone (Bello et al., 2019) while C – H aromatic combination bond is found in 1994.1 cm^{-1} wave length. The band with intensity that relate to C≡C stretch, alkyne bond is noticed in wave length 2083.6cm^{-1} (2260 – 2100 cm^{-1}) (Coates, 2000). Primary amine N – H bond stretch that is weak to medium broad band is found in 3269.9cm^{-1} wave length (Coates, 2000). The existence of aromatic combination, and amine bond groups that is found in the locust bean pod extract suggest it to be a good corrosion inhibitor to mitigate oxidation reaction on aluminium metal surface in hydrochloric acid environment. The presence of alkaloids, phenolic compounds, flavonoids, and tannin in the locust bean pod also favour its inhibitory potential, these constituents have been established in literatures for green corrosion inhibitors. Table 4 denotes the elemental composition of the aluminium metal used for the corrosion process. It can be seen that aluminium had the highest percentage composition in comparison to other elements present in the metal.

Table 3: Phytochemical Analysis of Locust Bean Pod Extract

Constituent	**Parameter indicator**
Saponin	+
Reducing sugar	-
Alkaloids	+
Protein (Amino acids)	+
Steroids	+
Tannins	+
Flavonoid	+
Anthraquinones	-
Phenolic compound	+
Terpenoids	+
Carbohydrates	+

Source: Okewale and Adedokun, (2022)

Keys: (+) indicates present, (-) indicates absent

Table 4: Chemical Composition of the Aluminium metal

Elements	Weight %
Silicon	0.34
Zinc	0.081
Copper	0.09
Manganese	1.070
Iron	0.591
Aluminium	97.828

Statistical Estimation of the Second Order Quadratic Model of CCD Response Surface Methodology

Testing of statistical estimates of the second order quadratic model was performed via analysis of variance (ANOVA) as depicted in Table 5. The F – value is employed to check how significant the model was. The high level of F – value (38.92) and p – value < 0.0001 indicated the quadratic model employed was adjudged to be significant. Thus, this is an indication that the data obtained experimentally is represented well by the quadratic model of second order used. The standard deviation value (0.068) is attained as seen in Table 7. The determination coefficient (R^2) which is described as the fraction of the individual parameter difference to the total variant of the parameters considered, this is utilized to measure fitness degree of the model. Joglekar *et al*., (1987) opined that a good model fit should give a coefficient of correlation (R^2) of at least 0.8. Coefficient of correlation/determination (R^2) value (0.9749) was realized for the model that is closer to 1, suggesting that the actual experimental values are closer to the predicted values exploited for the experimental design, this signify that the model is adjudged to be accurate (Mohd and Rasyidah, 2010). The results from this study has revealed the selected variables/ factors were sufficiently signified by the model obtained. However, this also portrayed an actual relationship among the factors selected in the experiment. This explained that 97.49 % of the overall variation in the loss of aluminium steel weight in the locust bean pod extract inhibitor can be linked to the variables examined experimentally. The p – values were used to check the implication of each of the coefficient in the model. An adequate precision ratio of 22.554 was attained, this is a sign of an adequate signal to noise ratio. It can also be suggested that the model can be used to route the design space. Precision ratio value obtained established the adequacy of the signal model.

The goodness – of – fit of the regression equation was measured using the adjusted coefficient of determination (R^2). The predicted R^2 value of 0.8557 which is an indication of the model power in response to predicted values from the experiment. The coefficient of variation (CV) for the standard deviation of the mean and experimental data is 12.43 %, this show that 87.52% of the experimental data were well correlated to each other. It can also be explained that this is an improved reliability, variation of experimental numbers and exactness of the experiments carried out (Li et al., 2011; Rodrigues et al., 2012). However, reproducible of the data value was checked from coefficient of variation value obtained which is lesser than 15 %. A p-value <0.05 specifies the model is statistically significant, although a value >0.1000 denotes that the model is insignificant (Zhang and Zheng, 2009). Significance of each coefficient is as well confirmed using the Probability value (P – value) and proportion of the mean square value (F – value) at 95% confidence interval level. It can be discerned that the corrosion inhibition of aluminium steel metal using locust bean pod inhibitor was substantially altered by (X_1, (p value 0.0061), X_2, and X_4, p<0.0001) linear terms but exposure time and concentration of locust bean pod inhibitor has a good synergestic effect on the weight loss of aluminium metal. It is obvious that the interaction terms (X_1X_4) are significant as well at the probability level of (p<0.05) while exposure time and temperature, concentration of HCl and concentration of locust bean pod inhibitor, concentration of HCl and temperature, concentration of locust bean pod extract and temperature have positive synergestic consequence on weight loss of aluminium metal as well as the quadratic terms of second order (X_2^2, and X_3^2) were likewise significant at the probability level (p<0.05). It suggest a positive interfaces among all the process variables considered which were noted to be the basic factors influencing the rate of corrosion, and weight loss of aluminium metal studied. Response Surface Methodology (RSM) model for the weight loss of aluminium metal using locust bean pod extract was optimized using the desirability function of Response Surface Methodology of State Ease statistical package. The optimization objectives used is as shown in Table 6. Statistical estimates of the Central Composite design is as presented in Table 7. Optimum conditions predicted from the quadratic model as depicted in Table 8, were locust bean pod extract concentration (111.98 ppm), exposure time (6.95 hours), temperature (64.12 ^oC), and HCl concentration (1.50 M) that correspond to aluminium metal weight loss of 1.08187 g. These values were subsequently substantiated experimentally while an average value of 1.19 g was obtained for loss in weight of aluminiium metal from three replicates, this was in tandem with optimum result envisaged by the regression model.

Table 5: Results of ANOVA Quadratic Model Regression Equation

Sources	Sum of squares	DF	Mean square	F - Value	P - value
Model	2.49	14	0.18	38.92	<0.0001
Time	0.048	1	0.048	10.43	0.0061
Concentration of HCl	2.06	1	2.06	450.13	<0.0001
Concentration of inhibitor	0.011	1	0.011	2.37	0.1463
Temperature	0.22	1	0.011	47.31	<0.0001
Time and Conc. of HCl	9.000E-006	1	9.000E-006	1.971E-003	0.9652
Time and Conc. of inhibitor	3.025E-003	1	3.025E-003	0.66	0.4293
Time and temperature	0.040	1	0.040	8.76	0.0103
Conc. of HCl and inhibitor	6.250E-004	1	6.250E-004	0.14	0.7169
Conc. of HCl and Temp	2.025E-003	1	2.025E-003	0.44	0.5162
Conc. of inhibitor and Temp	1.600E-003	1	1.600E-003	0.35	0.5633
Time²	0.026	1	0.026	5.64	0.0324
Conc. of HCl²	9.490E-003	1	9.490E-003	2.08	0.1714
Concentration of inhibitor²	5.455E-003	1	5.455E-003	1.19	0.292
Temperature²	0.055	1	0.055	12.09	0.0037
Residual error	0.064	14	4.566E-003		
Lack of fit	0.064	10	6.392E-003		
Pure error	0.00	4	0.00		
Corelation Total	2.55	28			

The experimental testing of full quadratic model is stated by the polymer equation of second order in term of coded variables below as equation 6:

$$Y= -1.96610+0.19028x_1+0.34167x_2-0.00497400x_3+0.056189x_4-0.001x_1x_2+0.000183333x_1x_3-0.00222x_1x_4+0.0005x_2x_3+0.003x_2x_4+0.00002667x_3x_4-0.007x_1^2+0.15300x_2^2+0.0000116x_3^2-0.00041x_4^2 \quad (6)$$

where, Y is the weight loss (g), x_1 is time of exposure (hrs), x_2 is hydrochloric acid concentrratioin (M), x_3 is concentration of locust bean pod extract as inhibitor (ppm), and x_4 is the temperature (^oC). After eliminating the insignificant variables the resulting final equation utilized for optimization is as given in equation 7.

$$Y=-1.96610+0.19028x_1+0.34167x_2+0.056189x_4-0.00222x_1x_4+0.007x_1^2+-0.00041x_4^2 \quad (7)$$

Table 6: Objectives of Optimization

Constraints	Goal	Lower limit	Upper limit
Time of exposure, (hrs)	in range	2	8
Inhibitor concentration, (ppm)	in range	0.5	1.5
Hydrochloric acid concentration, (M)	in range	20	120
Temperature, (^{o}C)	in range	35	65

Table 7: Statistical estimates of CCD

Parameters	**Value**
Standard deviation	0.068
Mean	0.54
Coefficient of variation (%)	12.43
Coefficient of determination (R^2)	0.9749
Predicted Coefficient of determination (R^2)	0.8557
Adjusted Coefficient of determination (R^2)	0.9499
Adequate precision	22.554

Table 8: Optimum Values

Constraints	**Optimum Values**
Time of exposure, (hrs)	6.95
Inhibitor concentration, (ppm)	111.98
Hydrochloric acid concentration, (M)	1.50
Temperature, (^{o}C)	64.12
Weight loss, (g)	1.08187

The normal values of residuals and internalized student values, predicted and experimental data on the loss in weight (g) of aluminium steel, were investigated also to determine their correlation this is shown in figures 2 and 3 respectively. Plot of residuals between the normal probability (%) and residuals of internally studentized is gotten and depicted as figure 2. In this model, the residuals was checked to establish how well the model suits the postulations made for analysis of variance (ANOVA). The residuals resulting from internally studentized can use in quantifying the standard deviations disconnecting the experimental and predicted values. Figure 2 can also be seen to suggest the relationship between the theoretical percentiles and the sample percentiles which is approximately linear, this indicate that error terms are normally distributed indeed. It can also suggests a very good interactions between the predicted values and the experimental values obtained for the response (weight loss of aluminium metal), this also implied a strong predictive power of the model used. The set data points on the plot were discreetly distributed and extremely near to the horizontal point line as shown in figure 3 for the predicted and experimental data plot. This indicates an incredibly suitable correlation between both the predicted and experimental values obtained for the response (weight loss of aluminium metal). In like manner, this further confirmed the assumptions made that this data can be used to route the design space. The residual values of experimental data and number of runs used in the CCD was also plotted in figure 4. This was used to check the model adequacy in ensuring that it gives maximum approximation on relationship between the response and variables considered. The residuals from the least squares are veritable tool for adjudging the model adequacy. This result is an indication of good predictions of maximum response (weight loss) along with constant variance and quadratic model adequacy (Zhang et al., 2012).

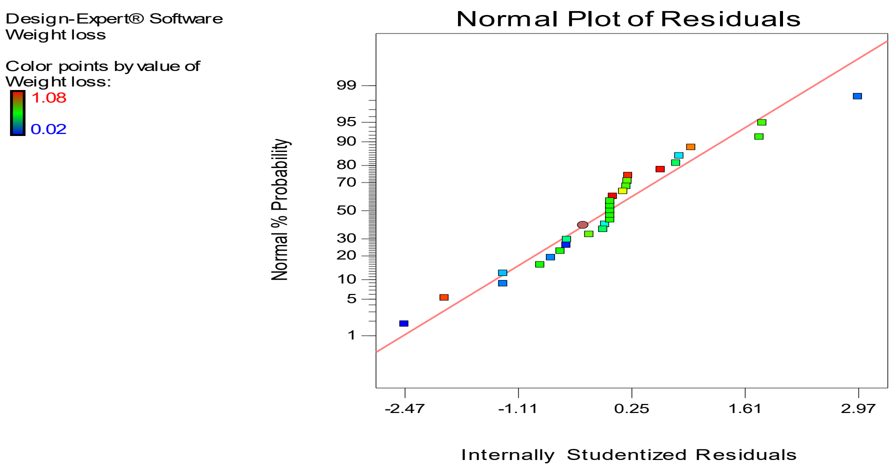

Figure 2: Values of the residuals versus the internally studentized residuals

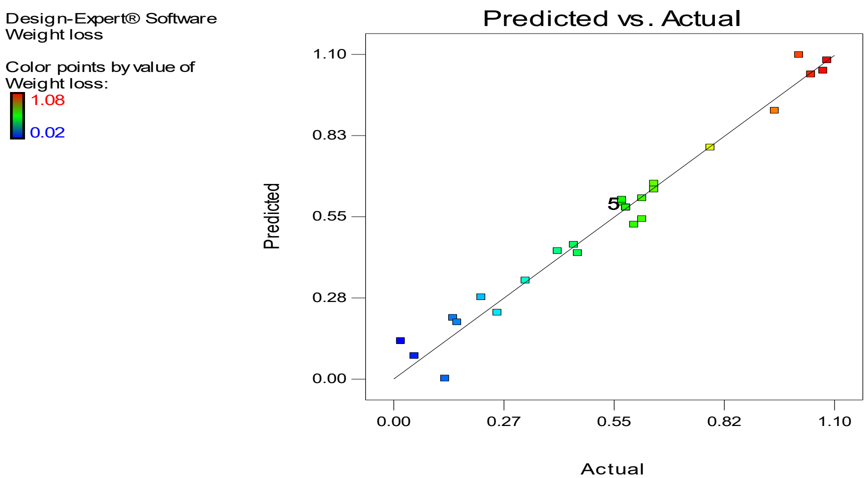

Figure 3: Predicted values of the model versus the experimental data values

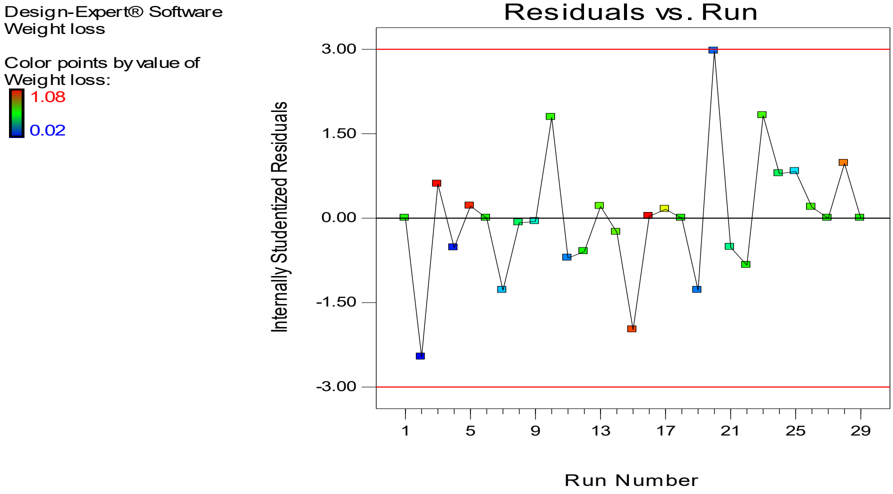

Figure 4: Residual values versus the actual numbers of experiment

Surface Response Plots

3-D surface response plots were given in Figures (5 – 10) centered on the investigation of the full quadratic model. These were exploited to provide an imperative proof on the behaviour of the aluminium metal corrosion system within the experimental design on the resulting weight loss.

Figure 5 described the attributes of locust bean pod extract concentration (x_3) and temperature (x_4) on the influence of aluminium loss in weight, it can be ascertained that the loss in weight of aluminium metal is reduced as locust bean pod extract concentration is increased at lower temperature. It can be implied that at lower temperature the electrochemical reactions is generally slower thereby reducing energy of ionisation to the reactions. This also asserted the positive synergy of temperature and inhibitor concentration as obtained in the model for aluminium metal corrosion. Figure 6 depicted the importance of time (x_1), and locust bean pod extract concentration (x_3), on weight loss of aluminium metal, it was noted that increase in time with higher locust bean pod extract concentration favoured a decreased in weight loss of aluminium metal. This is because with increased in concentration of inhibitor on the aluminium metal less metal surface will be exposed to corrosion process thereby reducing the weight loss of aluminium. This also confirmed the positive synergestic effect of these two terms on the loss in weight of aluminium metal corrosion. Figure 7 showed effect of time (x_1), and temperature (x_4) on weight loss of aluminium metal corrosion, it was revealed that lower temperature with increased in time favoured a higher weight loss of aluminium metal corrosion process studied. It can be explained that at lower temperature the inhibitor molecules were stable at lower temperature but the rate of dissolution of the aluminium metal in HCl medium is readily facilitated at elevated time of exposure. This also confirmed the non synergestic effect of these two variables on the loss in weight of aluminium metal corrosion. Figure 8 showed effect of locust bean pod extract concentration (x_3), and concentration of HCl (x_2) on loss in weight of aluminium metal corrosion, it was revealed that lower inhibitor concentration with lower HCl concentration favoured lower weight loss of aluminium metal corrosion process studied. It was further revealed that increased HCl concentration with increased locust bean pod extract concentration favoured higher weight loss of aluminium metal. The trend is due to the fact that the number of hydrogen ions which is the active species in HCl are increased, as the concentration of acid is increased which ultimately lead to increase in weight loss of aluminium metal. It also mean that the barrier energy of oxidation reaction decrease as the concentration of hydrochloric acid is increase and activated complex was formed faster with increase in acid concentration (Khadom et al., 2009).

Figure 9 showed effect of HCl concentration (x_2), and temperature (x_4) on weight loss of aluminium metal corrosion, it was discovered, as HCl concentration is increased along side temperature the loss in weight of aluminium also increased because elevated temperature raises the rate of both diffusion and reaction rate. This diffusion influences the delivery of oxygen to the aluminium metal, this oxide makes a film of reacted oxide on aluminium surface and thus forms barrier in preventing further oxygen reaction at lower temperature but at higher temperature the diffusion rates of oxygen went up at at very high magnitudes thus giving rise to increase in weight loss experienced at higher temperature. Figure 10 indicate the effect of locust bean pod extract (inhibitor) concentration (x_3), and temperature (x_4) on weight loss of aluminium metal corrosion. It was seen that as the inhibiotor concentration is decreased with increased in temperature the loss in weight of aluminium also increased. It indicates that at lower locust bean pod extract concentration, more parts of the metal surface is susceptible to oxidation reaction thereby making the rate of corrosion to be faster on the aluminium metal surface.

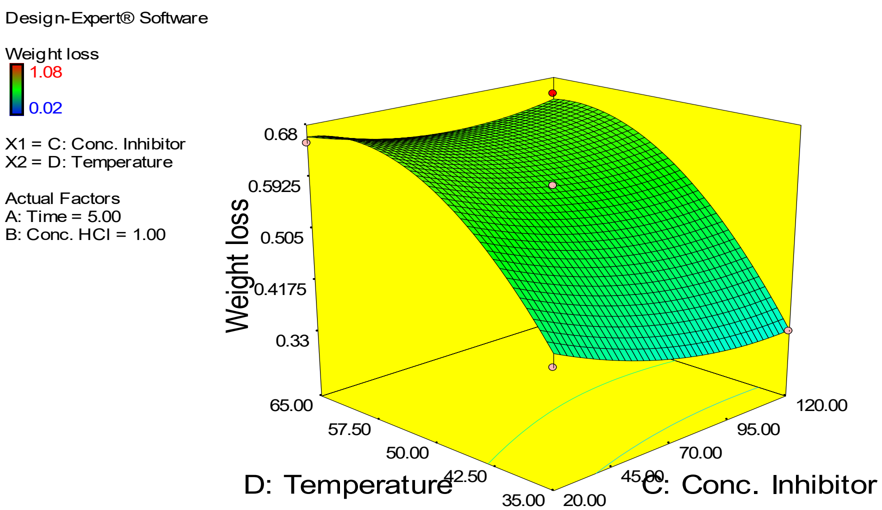

Figure 5: Surface Plot for the influence of locust bean pod extract concentration, temperature, and interface with loss in weight of aluminium.

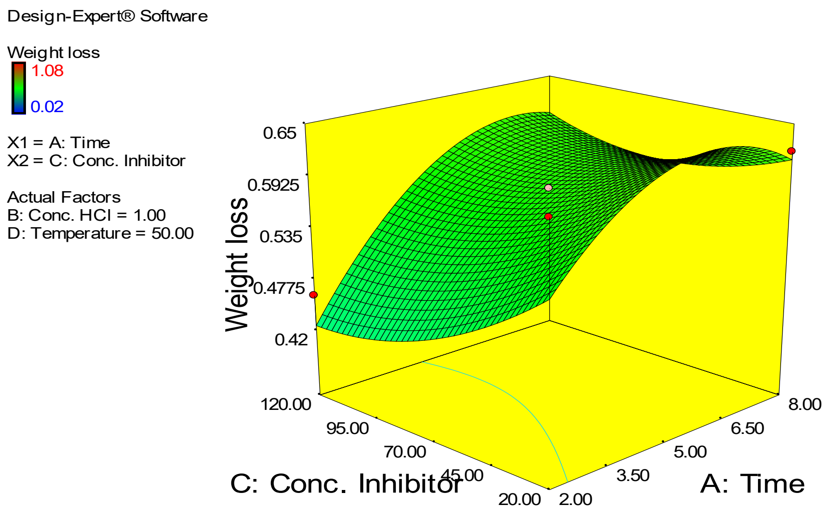

Figure 6: Surface 3 – D Plot for the influence of locust bean pod extract concentration, time, and interface with weight loss of aluminium.

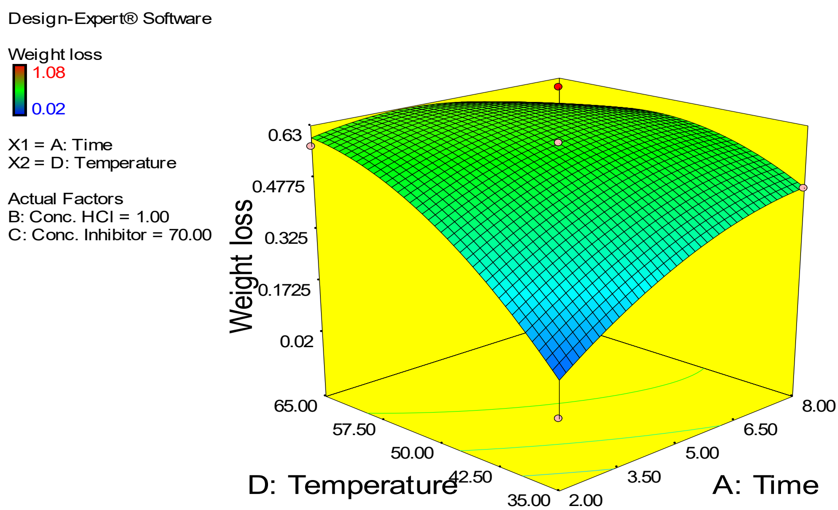

Figure 7: Surface Plot for the influence of temperature, time, and interface with loss in weight of aluminium.

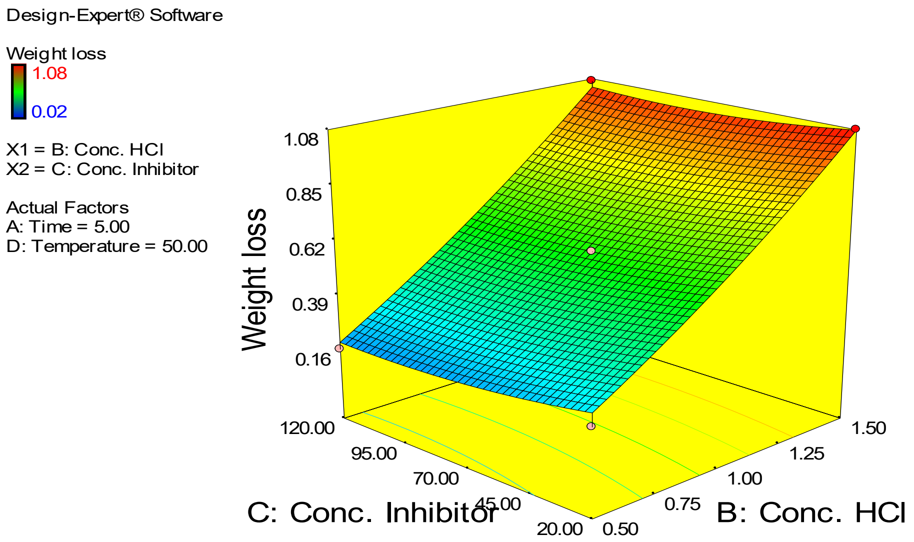

Figure 8: Surface Plot for the influence of locust bean pod extract, concentration of HCl, and interface with weight loss of aluminium.

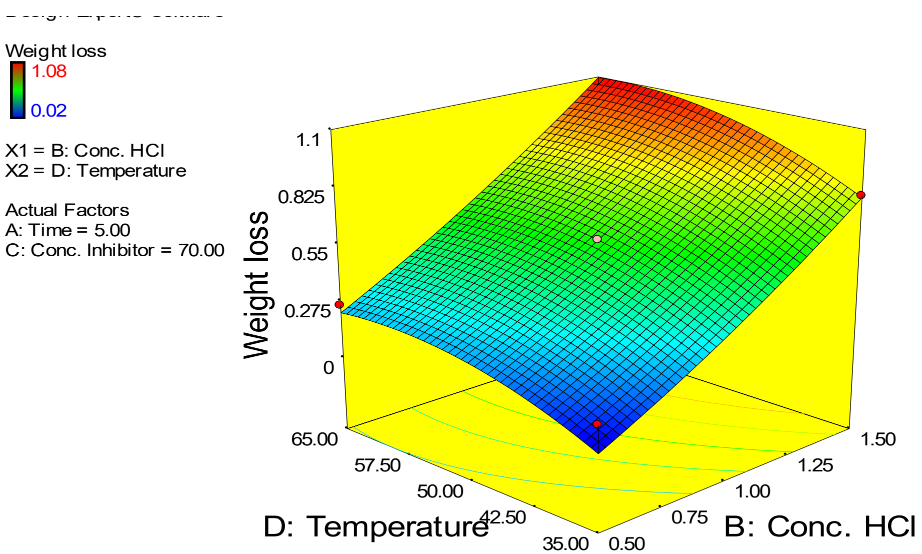

Figure 9: Surface 3 – D Plot for the influence of HCl concentration, temperature, and interface with loss in weight of aluminium.

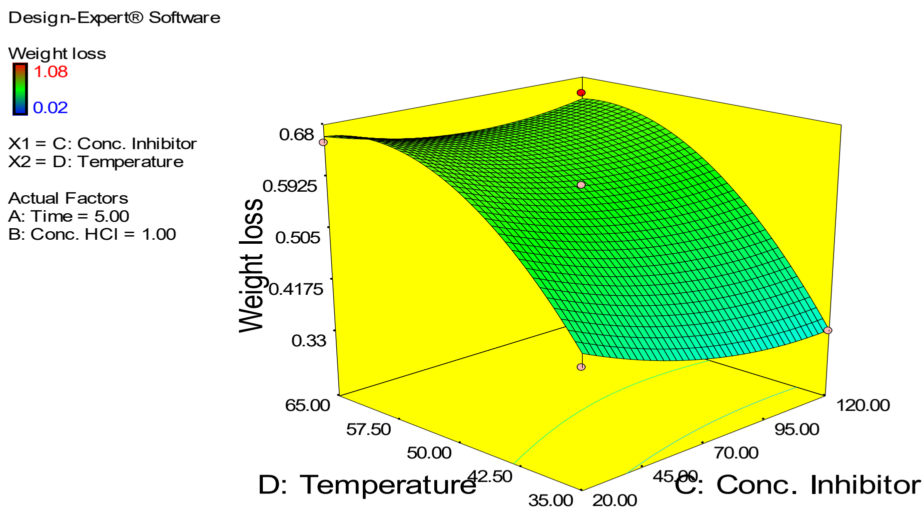

Figure 10: Surface Plot for the influence of locust bean pod extract concentration, temperature, and interface with weight loss of aluminium.

Corrosion rate, concentration of inhibitor, and time of exposure efect on Aluminium metal

Figures 11 and 12 depicted the rate of corrosion of aluminium metal with time of exposure that ranges from 48 hrs to 432 hrs at various inhibitors concentrations for 0.5 M HCl and 1.5 M HCl media. It can be seen that rate of corrosion decreases with increase in concentration of locust bean pod extract and also decrease as time of exposure is increased in both acid media. This indicate that the rate of corrosion penetration on aluminium metal is reduced. The decrease in corrosion rate of aluminium metal with increase in locust bean pod extract concentration, can said to occur as a result of the adsorption of larger molecules of the extract on the metal surface, this phenomenon occurs when a thin film of the locust bean pod is formed on the aluminium metal surface either by the interaction or process of adsorption. This thin protective film is mostly formed by the adsorption of locust bean pod on the positive sites formed on aluminium surface due to electrons liberation in the anodic process. This protective coating will isolate the aluminium metal from the HCl medium thereby lowering the rate of corrosion. For this corrosion process anodic reaction is suggested as the rate determining in this corrosion process corroborating the works of (Buoklah et al., 2005; Hassan, and Zaafarany, 2013; Iyeni and Obemure, 2020). It was also observed that the rate of corrosion also decrease with increase in HCl concentration.

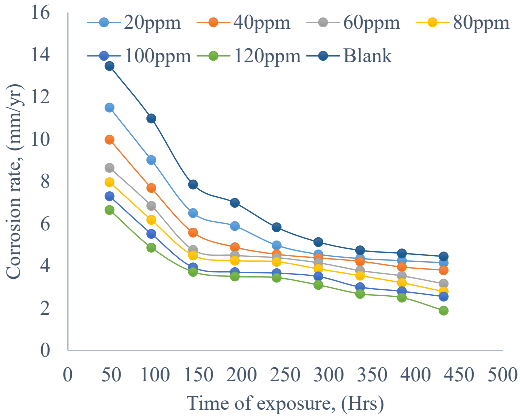

Figure 11: Corrosion rate versus time of exposure at 0.5 M HCl

Figure 11: Corrosion rate versus time of exposure at 0.5 M HCl

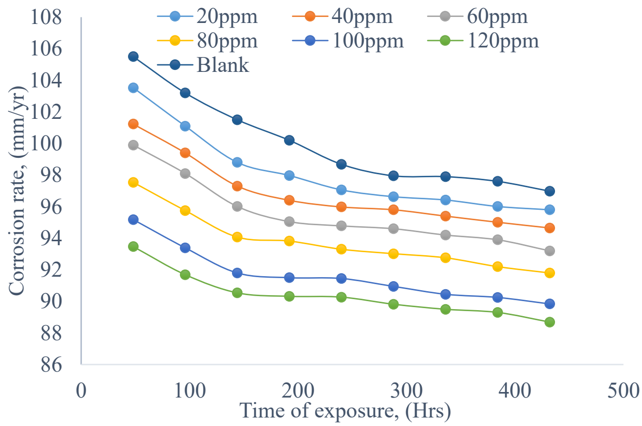

Figure 11: Corrosion rate versus time of exposure at 1.5 M HCl

The effect of HCl concentrations on the rate of aluminium metal corrosion in the presence and absence of locust bean pod extract inhibitor concentrations, at different time of exposure is as shown in Tables 9 and 10. It was observed that the rate of corrosion increase with acid concentration but it decrease with increase in time of exposure. The lower corrosion rate experienced with increased in time of exposure is as a result of the passive aluminium metal layer which may have been damaged by the corrosive chloride ions (Desiati et al., 2018). The increase in rate of corrosion noticed at 1.5 M HCl in comparison to 1 M HCl is attributed to the fact that increase in acid concentration leads to increase in rate of reaction which subsequently leads to the evolution of hydrogen ions. It can be seen that the highest rate of corrosion values were 105.50 mm/yr and 103.35 mm/yr, for blank and 20 ppm inhibitor concentration respectively at 1.5 M HCl concentration.

Table 9: Corrosion rate in mm/yr for aluminium metal at 1 M HCl

Time of exposure (Hrs)	20 ppm	40 ppm	60 ppm	80 ppm	100 ppm	120 ppm	Blank
48	11.5	9.98	8.65	7.97	7.30	6.65	13.47
96	9.02	7.69	6.85	6.18	5.52	4.87	10.99
144	6.50	5.58	4.76	4.50	3.93	3.72	7.86
192	5.89	4.89	4.50	4.25	3.71	3.50	6.99
240	4.98	4.55	4.39	4.20	3.66	3.45	5.83
288	4.55	4.38	4.15	3.86	3.50	3.10	5.13
336	4.35	4.22	3.78	3.54	3.00	2.68	4.74
384	4.25	3.95	3.53	3.20	2.80	2.50	4.60
432	4.15	3.80	3.16	2.79	2.55	1.89	4.45

Table 10: Corrosion rate in mm/yr for aluminium metal at 1.5 M HCl

Time of exposure (Hrs)	20 ppm	40 ppm	60 ppm	80 ppm	100 ppm	120 ppm	Blank
48	103.53	101.23	99.90	97.54	95.18	93.47	105.50
96	101.10	99.40	98.10	95.75	93.39	91.69	103.20
144	98.80	97.30	96.01	94.07	91.80	90.54	101.50
192	97.97	96.40	95.05	93.82	91.50	90.32	100.20
240	97.06	95.98	94.78	93.30	91.45	90.27	98.68
288	96.63	95.80	94.60	93.02	90.95	89.82	97.95
336	96.42	95.40	94.20	92.76	90.45	89.50	97.90
384	96.01	95.01	93.90	92.20	90.25	89.30	97.60
432	95.80	94.65	93.20	91.80	89.84	88.69	96.98

CONCLUSION

The potential of Locust bean pod as a corrosion inhibitor on aluminium metal was undertaken in this study. The phytochemical constituent and FTIR spectroscopy analysis exposed the inhibitive property that is inherent in locust bean pod. Corrosion rate of aluminium metal was found to decrease with increase in time of exposure but conversely decrease with increase in inhibitor concentration. The resultant effects of locust bean pod extract concentrations, process time, hydrochloric acid concentration and temperatures on the weight loss of aluminium metal were determined using Central Composite Design of RSM. It was corroborated that the linear terms variables that were significant are time, hydrochloric acid concentration, and temperature while the interactive terms of time and temperature were considered significant on weight loss of aluminium metal investigated. The statistical estimates showed that the errors are normally distributed, the optimum process conditions were validated

thrice in replicates, 1.19 g of aluminium weight loss was obtained.

REFERENCES

Abeng, F. E. Idim, V. D. Nna, P. J. (2017). Kinetics and Thermodynamic Studies of Corrosion Inhibition of Mild Steel Using Methanolic Extract of Erigeron floribundus (Kunth) in 2 M HCl Solution, World news of natural sciences, (**10**):26-38.

Adesina, O. A. Abdulkareem, F. Yusuff, A. S. Lalaa, M. and Okewale, A. O. (2019). Response surface methodology approach to optimization of process parameter for coagulation process of surface water using Moringa oleifera seed, South African Journal of Chemical Engineering, https://doi.org/10.1016/j.sajce.2019.02.002, **(28):**46 – 51.

Bello, O. S., Adegoke, K. A., Sarumi, O. O., and Lameed, O. S., (2019). Functionalized locust bean pod (Parkia biglobosa) activated carbon for Rhodamine B dye removal, Heliyon, (5) e02323.

Betiku, E. and Adesina, O. A. (2013). The statistical approach to the optimization of citric acid production using filamentous fungus Aspergillus Niger grown on sweet potato starch hydrolysate, Bioresource Bioenergy, **(55):**50 – 354.

Bouklah, M., Hammouti, B., Benhadda, T. and Benkadour, M., (2005). Thiophene derivatives as effective inhibitors for the corrosion of steel in 0.5 M H_2SO_4, Journal of Applied Electrochemistry, Volume **(35):** 1095-1101.

Coates, J., (2000). Interpretation of infrared spectra, A practical approach in Encyclopedia of analytical chemistry, Ed. Meyers, John Wiley and Sons Ltd, Chichester, 10815 – 10837.

Davis, J. R. (1999). Corrosion of aluminum and aluminum alloys, Materials Park, OH: ASM International

Desiati, R. D., Sugiarti, E., and Zaini Thosin, K. A., (2018). Effect of chloric acid concentration on corrosionbehaviour of Ni/Cr coated on carbon steel, Proceedings of the international seminar on metallurgy and materials, 020018 – 3.

Eugene Uwiringiyimana, Donnell, P. S. Ifeoma, V. J. and Feyisayo, V. A. (2016). The effect of corrosion inhibitors on stainless steels and aluminium alloys, African Journal of Pure and Applied Chemistry, **10(2)**:23-32.

Fasogbon, S. K., Wahaab, A. B., and Oyewola, M. O., (2016). Thermal comfort characteristics of some selected building materials in the regional setting of Ile-Ife, Nigeria, J. Nat. Resour. Develop., 54–58.

Femiana, G. Wahyono, S. and Rudy, S. (2018). Comparation of the analytical and experimental models of 304SS corrosion rate in 0.5 M H_2SO_4 with bee wax propolis extract, Engineering Review, **(38)2**:182 – 188.

Hassan, R., M., and Zaafarany, I. A., (2013). Kinetics of corrosion inhibition of aluminium in acidicmedia by water – soluble natural polymeric pectates as anionic polyelectrolyte inhibitors, Materials (Basel), **6(6):** 2436 – 2451.

Iyeni, E., and Obemure, C. O., (2020). Effect of inhibitor concentration and immersion time on the corrosion rate and inhibition efficiency of AISI 1019 steel in inhibited sea water environment, American journal of mechanical and materials engineering, **4(3)**: 66 – 80.

Joglekar, A. M. and May, A. T. (1987). Product excellence through design of experiments, Cereal foods world, **(32)**: 857.

Khadom, A. A., Yaro, A. S., and Kadum, A. H., (2009). The effect of temperature and acid concentration on corrosion of low carbon steel in Hydrochloric acid media, American Journal of Applied Sciences, **6(7):** 1406.

Li, J. Jha, A. K. and He, J. (2011). Assessment of the effects of dry anaerobic co –digestion of cow dung with waste water sludge on biogas yield and biodegradability, International Journal of Physical Science, **(6)15**:3723.

Mohd, A. A. and Rasyidah, A. (2010). Optimization of malachite green by KOH – modified grape fruit peel activated carbon: Application of response surface methodology, The chemical engineering journal, 751 – 988.

Nwigbo, S. C., Okafor, V. N., and Okewale, A. O, (2012). Comparative study of elaeis guiniensis exudates (palm wine) as a corrosion inhibitor for mild steel in acidic and basic solutions, Research journal of applied sciences, engineering and technology, **4(9):** 1035 – 1039.

Okewale, A. O., and Adedokun, J., (2022). Locust bean (*parkia biglobosa*) pod extract as corrosion inhibitor on aluminium in acidic media its adsorption isotherm models, Nigerian Journal of Scientific Research, **21(1):** 103 – 104.

Okewale, A. O. and Adebayo, A. T. (2020). Adsorption and thermodynamics studies of corrosion inhibition on carbon steel using pumpkin pod extract (*Telfairia occidentalis*), arid zone journal of engineering, technology and environment, **(16)2:** 395 – 406.

Okewale, A. O. Omoruwuo, F. and Adesina, O. A. (2019). Comparative Studies of Artificial Neural Network (ANN) and Response Surface Methodology (RSM) Predictive Capacity on Corrosion Inhibition of Mild Steel using Water Hyacinth as Inhibitor, FUW Trends in Science and Technology Journal, Vol., **(4)**2**:** 433 – 439.

Omoruwou, F. Okewale, A. O. and Owabor, C. N. (2017). Statistical analysis of corrosion inhibition of water hyacinth, Journal of Environmental and Analytical Toxicology, **(7):**34 – 39.

Revie, R. W., and Uhlig, H. H. (2008). Corrosion and Corrosion Control, In Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering: Fourth Edition. John Wiley & Sons, Inc. https://doi.org/10.1002/9780470277270.

Revie, R. W., (2011). Uhlig's Corrosion Handbook, In R. W. Revie (Ed.), Uhlig's Corrosion Handbook: Third Edition, John Wiley & Sons, Inc. https://doi.org/10.1002/9780470872864.

Rodrigues, R. C. Kenealy, W. R. Dietrich, D. and Jeffries, T. W. (2012). Response surface methodology (RSM) to evaluate effects on corn stover in recovering xylose by DEO hydrolysis, Bioresource Technol., **(108):**134 – 139.

Sylla, S. N., Samba, R. T., Neyra, M., Ndoye, I., Giraud, E., Willems, A., De Lajudie, P., Dreyfus, B., (2002). Pterocarpus erinaceus, Biosystems 583, 572–583.

Teklehaimanot, Z., (2004). Exploiting the potential of indigenous agroforestry trees: Parkia biglobosa and Vitellaria paradoxa in sub-Saharan Africa, Agrofor. Syst., 207–220.

Wang, M., Wang, J. Tan, J., X. Sun, J. F., and Mou, J. I., (2011). Optimization of ethanol fermentation from sweet sorgum juice using response surface methodology, Energy sources, **(33)12:**1139 – 1146.

Zhang, Z., and Zheng, H., (2009). Optimization for decolorization of azo dye acid green 20 by ultrasound and H_2O_2 using response surface methodology, Journal of Hazardous Materials, **(172):** (2-3), 1388 – 1393.

Zhang, Yun – jian, Li, Q., Zhang, Yu-xiu, Wang, Dan, and Xing, Jian-min, (2012). Optimization of succinic acid fermentation with actinobacillus succinogenes by response surface methodology (RSM), Journal of Zhejiang University – Science B (Biomedicine and Biotechnology), 13 (2): 108.Handbook: Third Edition, John Wiley & Sons, Inc. https://doi.org/10.1002/9780470872864.