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Dangonyaro Leaf Extort as a Wonderful Corrosion Fighter of Mild Steel in HCl

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Abstract: *Effect of dangonyaro leaf extort (Azadirachta indica) as a oxidization inhibitor of M- steel were studied. This were studied at various concentrations of HCl of 0.1 mol L^{-1}, 0.3 mol L^{-1} and 0.5 mol L^{-1} of temperatures of 30°C, 40°C and 50°C. Infusion method of extraction was examined for the extract preparation. The inhibition efficiency of M- steel in 0.1, 0.3 and 0.5 mol L^{-1} HCl increases as the as the concentrations of extracts temperatures increased. Dangonyaro extracts is an excellent inhibitor for M- steel in HCl. The adsorption procedure of components of spent dangonyaro grounds extracts obeyed the Langmuir adsoption isotherm. R- surface technique in design expert software which was utilized to sketch the experiment for weight loss showed a good results.The result of Anova for the corrosion rate implies that the model is considerable . Mathematical models in terms of coded for the inhibition competence of dangonyaro leaf extort in HCl were obtained by employing RSM tools of expert design software. The predicted and measured inhibition efficiencies got proves that RSM approach was suitable for optimizing the oxidization inhibition process.*

Keywords: *Dangonyaro , M- steel, Corrosion, Inhibitor, Acid*

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I. Introduction

M- steel is a unique engineering materials use for structural and auto applications. All engineering materials mostly used for structural and automobile rusted easily when they come in contact with aggressive environments and this affects their stability in service. This effect on them is what we called corrosion. Hence, corrosion is viewed as the ruin of materials resulting from their exposure and interaction with surroundings [1] . Corrosion preventers are employed to reduced the speed of oxidization on metals and its alloys in contact with destructive environments. Environmentally safe inhibitors are needed [2], [3] and[4] . Inhibition outcomes of harmless compounds on the metal corrosion had be reported [2] H. Ashassi- Sorkhabi (et al., 2004 and 2005) had reported the inhibition outcome of amino acids on the steel and aluminum oxidization in acid media. Lot of works had been accounted for employing economic plants like Vernoni Amydalina (bitter leaf) extorts [5] .Nupa Fruticans Wumb. Extracts [6] ,and the juice of cocos nucifera [7]for the acid oxidization of mild steel.

Research into the use of inexpensive and environmental friendly compounds as oxidization inhibitors for mild steel has strengthen in current years [9-31]. Plant extracts are economical. They can be obtained by the process of extraction . The progress of scientific uses for food residues might decrease the quantity of waste abandoned and enhance the economic feasibility of suitable waste management choices.
In this study, inhibition action of M- steel in 0.1, 0.3 and 0.5 mol HCl solution has been examined at diverse temperatures 30^0, 40^0, 50^0 and 60^0C by weight loss technique and Response surface method in design expert. Inhibition efficiency (I.E %) were computed as follows:

$$(I.E\,\%) = \frac{\Delta WB - \Delta Wi}{\Delta WB} \text{ X } \frac{100}{1} \quad (1)$$

ΔW_B and Δw_i were the weight loss data of the metal coupons in the dearth and in company of the (inhibitors).[6] .

II. Experimental

2.1. MATERIAL PREPARATIONS

M- steel of thickness 0.1 cm employed for this study was bought at Onitsha bridge – head market. Mechanically press-cut into 2cm x 2cm coupons. The coupons were used as bought with no extra polishing. Surface treatment of the coupon entailed degreasing in ethanol and dehydrating in acetone [8] .Coupons were them kept in damp – free desiccators to prevent contagion prior to their use in the corrosion studies

2.2. Inhibitor preparation

Inhibitor utilized was Dangonyaro leaf extort. The leaves of dangonyaro plant was got at Fegge – Onitsha, Anambra State, Nigeria. The leaves were sun dried for three days. Dried leaves were ground to boost the surface area and kept in a blocked container. 30 grams of the ground dangonyaro leaves (fine : particule size of 0.85mm) were gauged and immersed in 100ml of distilled water for 48 h. The mix up was sieved at the end of the 48 h. The remains got was a blend of plant extract and distilled water. Extract got was weighed and stored for the corrosion studies. Five different concentrations of the leaves extract which include 2 g/l, 4 g/l, 6 g/l, 6 g/l, 8 g/l and 10 g/l were prepared.

2.3. Weight loss measurement

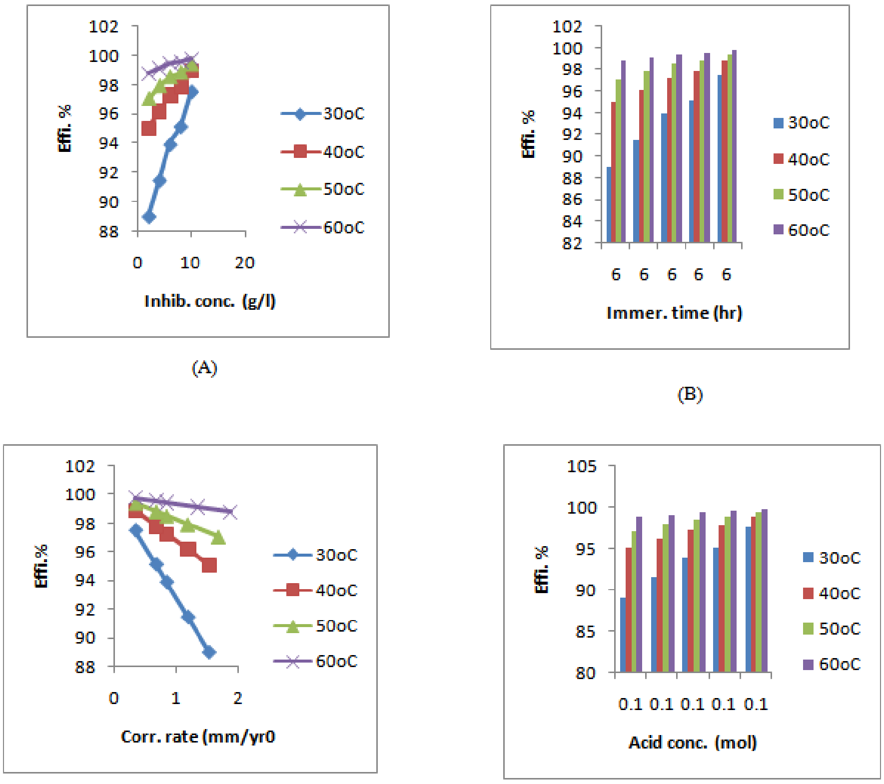
In weight loss method, 250 ml beakers containing blank solutions of 0.1, 0.3 and 0.5M of HCl were prepared. The test was performed in full immersion in the test solution uphold at 30^0, 40^0, 50^0 and 60^0C individually. Weighed metal coupons were poised in the beaker by the help of wooden bars and twines and submerged in a thermosated water bath set at a given equilibrated study temperature stated above. These coupons were retrieved at 24 – hour interval.

2.4. Weight loss method using response surface technique.

Response surface technique in design expert software was employed to designed the research for weight loss technique. Temperature, time, inhibitor concentration with medium concentration were the considered factors while corrosion rate, inhibition efficiency and surface coverage were the expected responses of the study. The RSM was employed to examine the responses. ANOVA and graphical analyses of the inhibition efficiencies were also carried out. Mathematical terms of the coded were got. Models in terms of coded factors were employed to make a forecasts on the response for the factor. Elevated levels of the factor were coded as + and the low levels of the factor were coded as – 1. Optimum inhibition parameter were obtained.

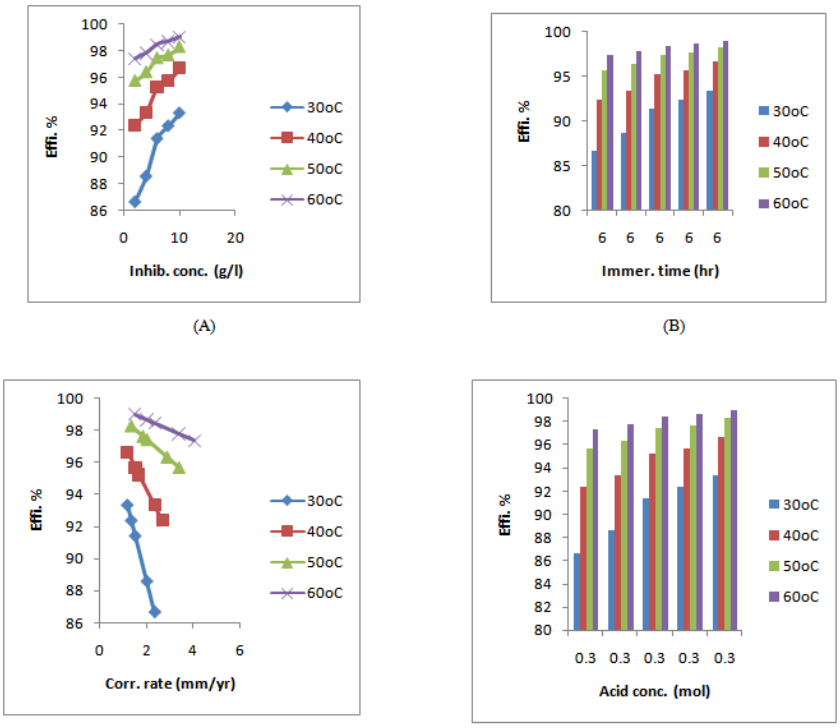
III. Results And Discussion

Corrosion of M- steel coupons in 0.1, 0.3 and 0.5 M HCl without and with dangonyaro leaves extracts were studied using gravimetric technique. The values of corrosion rate, inhibition efficiency and degree of surface coverage of M- steel corrosion in 0.1, 0.3 and 0.5M HCl, with different concentrations of dangonyaro leaf extract inhibitor as a functions of of time, (h), temperature (^0C), concentration (g/l) efficiency (%), and corrosion rate (mm/yr) are presented in Table: 1 and figures : 1 – 4 below



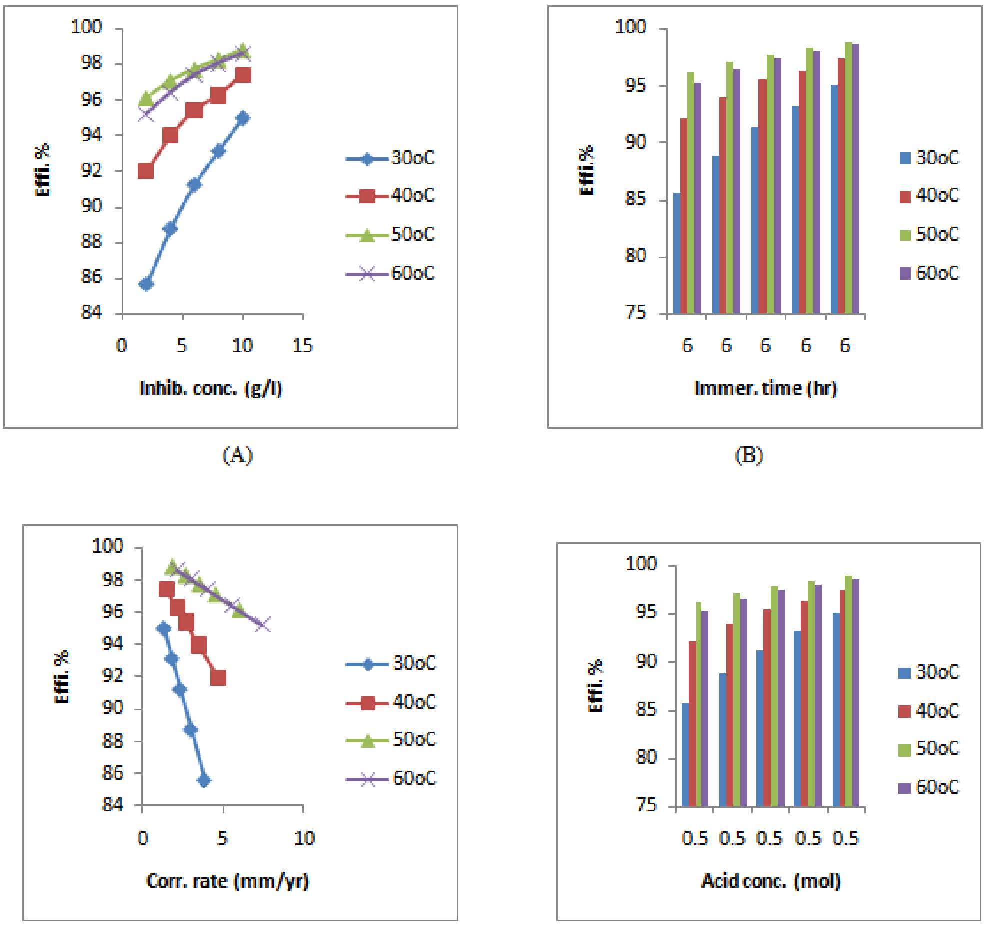
(C) (D)

Figure 1: Result of inhibitor concentration (a), immersion time (b), corrosion rate (c) and acid concentration (d) on the inhibition efficiency of M- steel in 0.1M HCl at different concentration of dangonyaro leaf extract inhibitor, and at varied temperatures.



(C) (D)

Fig. 2: Result of inhibitor concentration (a), immersion time (b), corrosion rate (c) and acid concentration (d) on the inhibition efficiency of mild steel in 0.3M HCl at different concentration of dangonyaro leaf extract inhibitor, and at varied temperatures.



(C) (D)

Fig. 3: Effect of inhibitor concentration (a), immersion time (b), corrosion rate (c) and acid concentration (d) on the inhibition efficiency of mild steel in 0.5M HCl at different concentration of dangonyaro leaf extract inhibitor, and at varied temperatures.

The figures showed the variations of inhibitor concentration against efficiency, immersion time against efficiency and acid concentration against efficiency for M- steel corrosion in 0.1, 0.3 and 0.3 M HCl and different concentrations of the inhibitor. Inspection of the figures and table reveal that corrosion rate was highest with M- steel coupons in 0.5 M HCl and lowest with that of 0.1 M HCl. However, in the presence of inhibited solution, corrosion rate of mild steel coupon decreased with increased in inhibitor concentration. This indicated that inhibitor actually inhibited the dissolution of M- steel in 0.1, 0.3 and 0.5 M HCl environment. Furthermore, there was decrease in corrosion rate with respect to concentration of acid. The less the concentration of acid, the less the rate of corrosion. The lowest corrosion rate of 0.34 (mm/yr) occurred at 0.1 M HCl which was the lowest concentration of acid studied. This could be due to the reduction in the strength of acid caused by arrest of molecules of the inhibitors . As a result, there was loss of power of the aggressive solution concentration of acid.

Inhibition efficiency of the inhibitors for M- steel corrosion of 0.1, 0.3 and 0.5 M HCl shown in the figures above indicated that inhibition efficiency improved with raise in concentration of the inhibitors. Maximum inhibition efficiency was detected at 10 g/l concentration of the inhibitor and at the highest temperature of 60^{0}C. This inhibitive effect of the inhibitors could be ascribed to adsorption of molecules of the inhibitors on the shell, displacing less stable molecules of water, hence, forming a barrier coat between the metal surface and aggressive solution [33]

TABLE 1: Calculated values of corrosion rates (MM/Yr), inhibition efficiency (%) and degree of surface coverage (Ө) for M- steel corrosion in 0.1, 0.3 and 0.5 M HCl at diverse concentrations of inhibitors (dangonyaro leaf extort) and at various temperatures.

Time (Hour) 6 Hr	Inhibitor Conc. (g/L)	Corrosion rate (mm/yr)				Inhibition Efficiency (%I)				Degree of Surface Coverage (Ө)			
		30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
0.5 M HCl	BLANK	26.94	58.93	155.23	155.23								
	2g/LOLE	3.87	4.71	6.06	7.41	85.63	92.01	96.1	95.23	0.86	0.92	0.96	0.95
	4g/LOLE	3.03	3.54	4.55	5.56	88.75	93.99	97.07	96.42	0.89	0.94	0.97	0.96
	6g/LOLE	2.36	2.69	3.54	4.04	91.24	95.44	97.72	97.4	0.91	0.95	0.98	0.97
	8g/LOLE	1.85	2.19	2.69	3.03	93.13	96.28	98.27	98.05	0.93	0.96	0.98	0.98
	10g/LOLE	1.35	1.52	1.85	2.19	94.99	97.42	98.81	98.59	0.95	0.97	0.99	0.99
0.3 Ml HCl	BLANK	17.68	35.36	78.79	155.23								
	2g/LOLE	2.36	2.69	3.37	4.04	86.65	92.39	95.72	97.4	0.87	0.92	0.96	0.97
	4g/LOLE	2.02	2.36	2.86	3.37	88.57	93.33	96.37	97.83	0.89	0.93	0.96	0.98
	6g/LOLE	1.52	1.68	2.02	2.36	91.4	95.25	97.44	98.48	0.91	0.95	0.97	0.98
	8g/LOLE	1.35	1.52	1.85	2.02	92.36	95.7	97.65	98.7	0.92	0.96	0.98	0.99
	10g/LOLE	1.18	1.18	1.35	1.52	93.33	96.66	98.29	99.02	0.93	0.97	0.98	0.99
0.1 M HCl	BLANK	13.81	30.81	56.57	155.23								
	2g/LOLE	1.52	1.52	1.68	1.87	88.99	95.07	97.03	98.8	0.89	0.95	0.97	0.99
	4g/LOLE	1.18	1.18	1.18	1.35	91.46	96.17	97.91	99.13	0.91	0.96	0.98	0.99
	6g/LOLE	0.84	0.84	0.84	0.84	93.92	97.27	98.52	99.46	0.94	0.97	0.99	0.99
	8g/LOLE	0.67	0.67	0.67	0.67	95.15	97.83	98.82	99.57	0.95	0.98	0.99	1
	10g/LOLE	0.34	0.34	0.34	0.34	97.54	98.9	99.4	99.78	0.98	0.99	0.99	1

3.1 The result of the weight loss method using RSM

Responses of the corrosion rate, inhibition efficiency and surface coverage to the factors of temperature, inhibitor concentration and medium concentration for corrosion inhibition of metals in media with ganyonyaro leaves extract is presented in Table 2. Data show the disparity of corrosion rate with temperature, inhibitor concentration and medium concentration of mild steel metal in acid medium HCl. Corrosion rate improved with raise in temperature and media concentration. Decrease in corrosion rate with raise in concentration of the inhibitor is an sign that the inhibitor dangonyaro leaf subdued the corrosion of M- steel in acid medium. Raise in the concentration enhances the inhibition efficiency and surface coverage. Also, inhibition efficiency diminishes as the temperature rises.

Dangonyaro leaf extract has better efficiency. High inhibition efficiency recorded in the medium may be attributed to the actions of protonated and molecular species. Some of the constituents of the inhibitors may have been adsorbed as protonated species and some molecular species [34].The high efficiency of gangonyaro leaves extract might be attributed to the occurrence of C- H bend, C- O functional group, $-CH_3$ bend, C = O stretch, C= O symmetric, X= C= Y, C ≡ N stretch, N- H stretch and Hydrogen – bonded O- H stretch contributed to this. This high values of the inhibition efficiencies indicated that the dangonyaro leaf used is good for the treatment of the metal surface. It has the capacity to inhibit corrosion when employed as corrosion inhibitor in metallic maintenance operations.

The variation of inhibition efficiency with concentration, temperature and time were further analyzed using mathematical models find out by response surface methodology (RSM) of the design expert software. RSM is an effective means to realize optimization by investigating and modeling the outcome of numerous variables and their reactions and finally optimizing the process. Analysis of the data will include the 3-D graphical respresentations of the relationship among inhibition efficiency and factors of concentration, temperature and time. The mathematical models generated will show inhibition efficiency as a role of concentration, temperature and time. The interactions among the factors of concentration, temperature and time will be identified.

Table 2 : The RSM result of the corrosion inhibition of St. in HCl by dangonyaro leaves extract.

Std	Run	Factor 1; A: Tempt. oC	Factor 2; B: Inhibior conc. (g/l)	Factor 3; C : Medium conc.(M)	Response 1; Corrosion rate (mm/yr)	Response 2; Inhibitor efficiency (%)	Response 3; Surface coverage (K)
4	1	60.00	10.00	0.30	1.52	99.02	0.99
13	2	45.00	6.00	0.30	1.85	96.92	0.93
12	3	45.00	10.00	0.50	1.68	98.92	0.99
9	4	45.00	2.00	0.10	1.59	96.15	0.96
5	5	30.00	6.00	0.10	0.84	90.07	0.9
15	6	45.00	6.00	0.30	1.85	96.92	0.93
16	7	45.00	6.00	0.30	1.85	96.92	0.93
11	8	45.00	2.00	0.50	5.39	96.54	0.97
17	9	45.00	6.00	0.30	1.85	96.92	0.93
1	10	30.00	2.00	0.30	2.36	86.65	0.87

2	11	60.00	2.00	0.30	4.04	97.4	0.97
8	12	60.00	6.00	0.50	4.04	90.03	0.9
7	13	30.00	6.00	0.50	2.36	91.24	0.91
10	14	45.00	10.00	0.10	0.34	99.21	0.99
3	15	30.00	10.00	0.30	1.18	93.33	0.93
14	16	45.00	6.00	0.30	1.85	96.92	0.93
6	17	60.00	6.00	0.10	0.84	99.46	0.99

3.2 Graphical Analysis of the Inhibition Efficiency, IE (%), as Determined using RSM

Examination of the inhibition efficiencies of dangonyaro leaves (inhibitors) of the metal in the acidic are presented in figures 5. The graphs of inhibition efficiency of the inhibitors of dangonyaro (steel in HCl) , are shown in figures 5. Plots of Normal Plots of Residuals versus Studentized Residuals were employed to check the worth of the models order. In all cases studied, the residuals versus studentized residuals gave linear graphs. Graphs (3-D surface plots) showed the liaison involving the factors and responses of the designed experiments. Factors consist of inhibitor concentration, temperature and time of the metal immersion. Response is the inhibition efficiency. Corrosion inhibition of metal steel and in acid medium HCl with plant extracts (dangonyaro leaf) showed that raise in concentration enhances the inhibition efficiency. Moreover, inhibition efficiency diminishes as temperature goes up. The surveillances are in harmony with earlier studies [35] .

Graphs of inhibition efficiency versus concentration, temperature and time are in quadratic forms. Further analysss of the data will addressed in terms of analysis of variance, mathematical models and optimization .The analysis of variance helped in identifying the models significance terms. The powers of the variables were used to confirm the quadratic models. The models displayed the inhibition efficiency of the inhibitors as a role of factors of concentration, temperature and time. The interactive behaviour of the concentration, temperature and time were also identified.

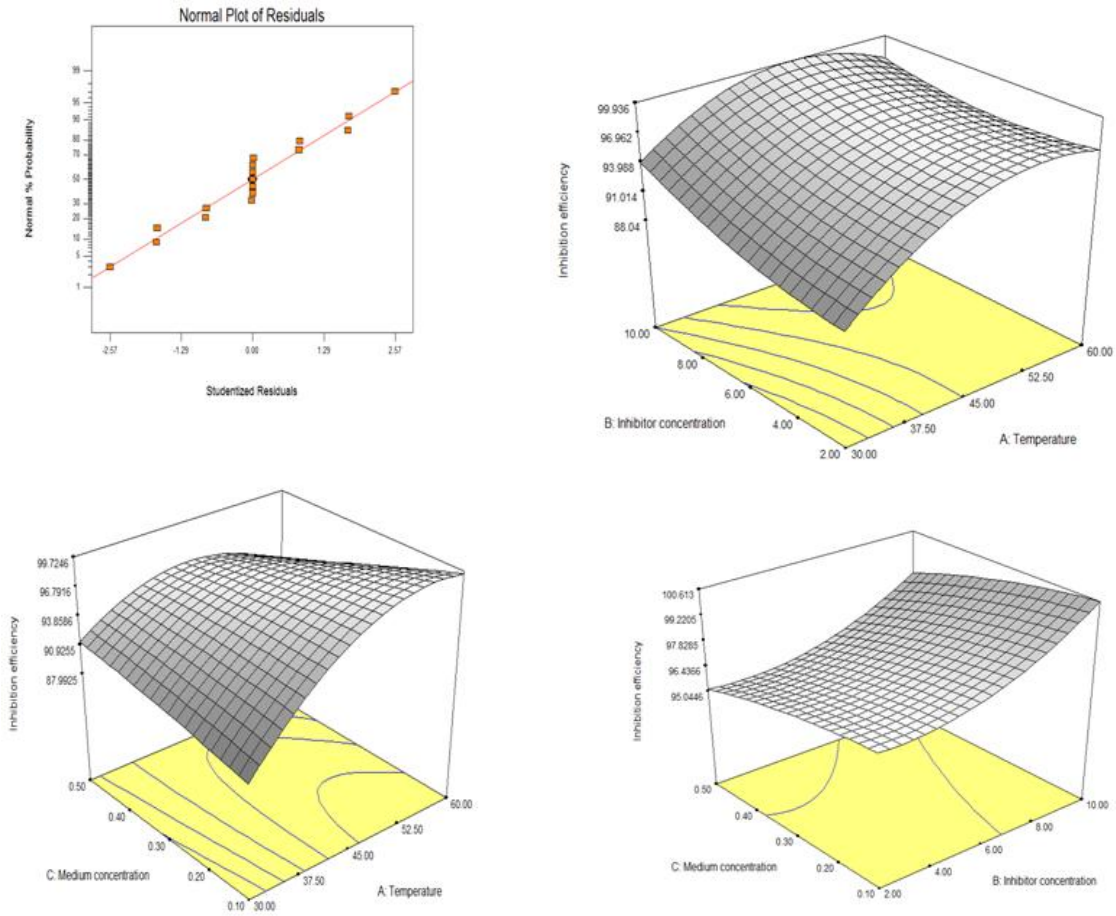


Fig. 5: IE (%) of dangonyaro leaves extracts as corrosion inhibitor of steel in HCl
a) Normal Plot of Residuals versus Studentized Residuals IE (%), b) IE (%) vs. inhibitor concentration and temperature, c) IE (%) vs. medium concentration and temperature, d) IE (%) vs. medium concentration and inhibitor concentration.

From the ANOVA for the corrosion rate of Steel in HCl by dangonyaro, the model F- worth of 8.97 implies the mobel is momentous (Table 6). There is only a 0.01 possibility that an F- worth this large could arise due to noise.Values of "Prob > F" less than 0.5000 validate that model terms are significant. In this case A, B, C, A^2, AB, AC, BC are momentous model terms. Values greater than 0.1000 indicate the model terms are momentous. The "Pred R-Squared" of -0.2762 is in reasonable agreement with the "Adj R-Squared" of 0.8177; the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. Ratio greater than 4 is desirable. The ratio of 10.180 in shows an adquate signal. This model can be employed to navigate the design space.

Table 6: ANOVA for the corrosion rate of Steel in HCl by dangonyaro.

ANOVA for Response Surface Quadratic model ; corrosion rate						
Analysis of variance table [Partial sum of squares – Type III]						
	Sum of		Mean	F	p-value	
Source	Squares	Df	Square	Value	Prob > F	
Model	210.98	9	23.44	8.97	0.0043	Significant
A- Temperature	75.77	1	75.77	29.00	0.0010	
B- Inhibitor conc	23.60	1	23.60	9.03	0.0198	
C- Medium conc.	8.32	1	8.32	3.19	0.1174	
A^2	64.45	1	64.45	24.67	0.0016	
B^2	5.03	1	5.03	1.92	0.2080	
C^2	0.40	1	0.40	0.15	0.7079	
AB	6.40	1	6.40	2.45	0.1615	
AC	28.09	1	28.09	10.75	0.0135	
BC	0.12	1	0.12	0.044	0.8394	
Residual	18.29	7	2.61			
Lack of Fit	18.29	3	6.10			
Pure Error	0.000	4	0.000			
Cor Total	229.27	16				
Std. Dev.	1.62		R-Squared			0.9202
Mean	95.45		Adj R-Squared			0.8177
C.V. %	1.69		Pred R-Squared			-0.2762
PRESS	292.59		Adeq Precision			10.180

3.3.Mathematical models of the inhibition efficiency

Mathematical models of inhibition efficiency

Mathematical models used for the inhibition efficiency of dangonyaro leaves extort as oxidization inibitor of metals in acid medium are shown in Equations 3. The model was obtained by employing RSM tools of expert design software. Each model showed the association between the inhibition efficiency (IE), inhibitior concentration (A), temperature (T) and time or day (C). Mathematical models in terms of coded factors were obtained using the optimization tool of the RSM. The models in terms of the coded factors predicted the answer for given levels of each factor.

Positive signs in the models indicated synergistic effect, whereas the negative signs siginified anatagonistic effect.

Model for corrosion inhibition of M- steel in HCl by dangonyaro leaves extort is;

$$IE = +96.92 +3.08 *A +1.72 *B + - 1.02 *C -3.91 *A^2 +1.09 *B^2 -0.31 *C^2 -1.27 *A *B -2.65 *A *C -0.17 *B *C \quad (2)$$

3.4Optimum Parameter for Corrosion Inhibition of Mild steel Metal

Data on Table 4 show the optimum inhibition concentration, optimum temperature, optimum time and optimum inhibition efficiency for M- steel metal in HCl medium. Analysis of the optimum inhibition efficiency of dangonyaro leaf extract showed 99.46%

Table 4 : Optimum parameter for corrosion inhibition of M- steel in HCl with dangonyaro leaf extort.

Media	Inhibitor (plant extract)	Optimum inhibitor conc. (g/l)	Optimum temperature oC	Optimum medium conc. (M)	Optimum inhibition efficiency (%)
HCl	Dangonyaro leaves	10	60	0.5	99.46

3.5Validation of the result

To verify the validity of result, further experiment was carried out. Condition for the concentration, temperature and time s listed in Table 5, with the forecasted and measured inhibition efficiency. As revealed in the Table 5, the measured inhibition efficiency was closed to the forecasted value. It illustrates that RSM approach was suitable for optimizing the oxidization inhibition process.

Table 5 : Result validation for corrosion inhibition of M- steel in HCl medium with plant extract

Media	Innhibitor (plant extract)	Inhibitor conc. (g/l)	Temperature (o C)	Medium conc. (M)	Predicted inhibition efficiency (%)	Measured inhibition efficiency (%)	Percentage error (%)
HCl	Dangonyaro leaves	10	60	0.5	99.46	99.78	0.32

IV. Conclusion

From this investigation, the following conclsion can be drawn

1. M- steel corrode in 0.1, 0.3 and 0.5 M HCl
2. The weight loss of M- steel in HCl depends on the concentration of the acid, it corroded and even dissolve in HCl without the incorporation of the dangonyaro leaf extract as inhibitor
3. Dangonyaro leaf extract is an excellent corrosion inhibitor for the corrosion in acidic medium and not scarce when looked for .
4. It does not cause heath hazard unlike most in organic inhibitors.

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