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Optimization Of The Inhibitive Properties Of Azadirachta Indica Seed Extract On The Corrosion Of Aluminium In Acid Medium

***Ekeke I. C., Osoka, E. C., Nwanja J. U. and Nze E.**
Department of Chemical Engineering, Federal University of Technology Owerri,
Imo State Nigeria
ifyekeke@yahoo.com
*Corresponding author

***Abstract*- Azadirachta indica seed extract (neem seed) was examined as an anti-corrosion agent for aluminum in hydrochloric acid medium using the gravimetric (weight loss) method. The inhibition efficiency was optimized by application of Response Surface Methodology (RSM) using Design Expert Software 11. Inhibitor concentration (0.2 g/l – 1.0 g/l), temperature (303 K – 343 K) and time (1hour - 5 hours) were the factors considered. An inhibition efficiency of 83.33% was obtained for one factor at a time study using weight loss method, at an inhibitor concentration of 1.0g/l. A quadratic model adequately described the inhibition process with concentration of inhibitor having a greater impact. Optimum inhibition efficiency of 84.763% was obtained at inhibitor concentration of 0.901 g/l, temperature of 317.521K and time of 3.898 hrs.**

Keywords—Corrosion, Azadirachta indica, RSM, Adsorption isotherm, Aluminum, Optimisation

INTRODUCTION

Aluminum structure corrodes as a result of electrochemical reaction with its environment. Pickling, descaling and cleaning are often carried out to prolong the life span of aluminum structures. Acid medium such as HCl used for such maintenance operations often corrodes the structures. The adverse consequences of corrosion are therefore considered a serious problem in industry, construction and civil services such as electricity, water and sewage systems [1]. Corrosion prevention and retardation are aimed at addressing these factors.

Much research has been carried out in the area of corrosion inhibition of metals by the use of biomass [2, 3, 4, 5, 6, 7**,** 8, and 9].

Optimisation is a viable tool in the selection of the best alternatives in any process. In the area of corrosion inhibition, for instance, it helps the researcher choose the best combination of concentration of inhibitor, time of inhibition and temperature of inhibition when carrying out corrosion inhibition studies.

Response Surface Methodology (RSM) is a widely used mathematical and statistical method for modelling and analyzing a process in which the response of interest is affected by various variables and the objective of this method is to optimize the response. RSM investigates an appropriate approximation relationship between input and output variables and identifies the optimal operating conditions for the system. Design of Experiments is the most important aspect of RSM and it aims at identification of the most suitable points where response should be well examined [10].

MATERIALS AND METHODS

Material Preparation: The aluminum sheet of composition Si (0.25%), Fe (0.02%), Zn (0.05%), Mn (0.04%) Mg (0.03%), V (0.04%), Ti (0.02%), Cu (0.03%), Cr (0.02%) and Al (99.5%), that was used for this study was mechanically cut into coupons of dimension $3\times3\times0.035$□□. The coupons were washed in distilled water, degreased in absolute ethanol, dried in acetone and preserved in a moisture-free desiccator.

Preparation of Plant Extract: Matured seeds of *Azadirachta indica* were harvested from the neem Garden at Federal University of Technology Owerri, Imo State, Nigeria. The seeds were washed and sun dried for 9 days. They were further reduced in size using electric grinder. 500g of the ground seeds were soaked in 1000ml of analytical grade ethanol in a 2-liter container for 48 hours. The resulting mixture was filtered using whatman No. 42 grade filter paper. The resulting solution of the *Azadirachta indica* seeds extract and the solvent were heated in a constant temperature water bath set at 80^{o}C in order to recover the extract. Five inhibitor test samples were then prepared by dissolving 0.1g/l, 0.2g/l, 0.4g/l 0.6g/l, 0.8g/l and 1.0g/l of the extract in 200ml of 0.5M HCl respectively.

Weight loss (gravimetric) measurement: The weight loss (gravimetric) method used by [11] was adopted in this study. It involves one-factor at a time study and Response Surface Methodology (RSM). The variation of weight loss was monitored periodically at various temperatures (303K, 313K, 323K, 333K and 343K) and in 0.5M HCl medium, in the absence and presence of various concentrations of the extract. At the appropriate time (over a 5-hour period at intervals of 1hour), the aluminum samples were taken out, immersed in acetone, scrubbed with a bristle brush under running water, dried and reweighed. The weight loss was calculated in grams as the difference between the initial weight and the weight after the removal of the corrosion product. The experimental readings were taken. The weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE) and degree of surface coverage were calculated using equations (1), (2), (3) and (4) respectively.

$$\Delta w = W_1 - W_2 \ (1)$$

$$C_R = \frac{W_1 - W_2}{Area \times time} \ (2)$$

where

C_R = Corrosion rate (mg/cm^{2}hr)

W_1 = initial weight of the coupons before corrosion (mg)

W_2 = weight after corrosion over a given time (mg)

$$IE\% = \frac{C_{R0} - C_{R1}}{C_{R0}} \times 100 \ (3)$$

$$\theta = \frac{C_{R0} - C_{R1}}{C_{R0}} \ (4)$$

where EI = Inhibition efficiency (%), C_{Ro} =uninhibited corrosion rate (mg/cm^2hr), C_{R1} = inhibited corrosion rate (mg/cm^2hr)

Different adsorption isotherms were used to determine the mechanism of the adsorption of the extract on the aluminum surface. Parameters of the Langmuir, Frumkin, Temkin and Flory-Huggins isotherms were obtained using equations (5), (6), (7), and (8) respectively, while equations (9) and (10) were used to determine the activation energy and heat of adsorption respectively.

$$\frac{logc}{\theta} = logC - logK \ (5)$$

$$\log\left[\frac{\theta}{(1-\theta)C}\right] = logK_{ads} + \frac{2\alpha\theta}{2.3030} \ (6)$$

$$\theta = \frac{2.303logK}{2a} - \frac{2.303logC}{2a} \ (7)$$

$$log\left(\frac{\theta}{C}\right) = logK + xlog(1-\theta) \ (8)$$

where C (g/l) is the inhibitor concentration, K is the adsorption equilibrium constant, α is a lateral interaction term describing the interaction in adsorbed layer, a is the attractive parameter and x is the size parameter, a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.

Considering the initial temperature (T_1) and the final temperature (T_2) for the corrosion inhibition process, and its corresponding corrosion rates; C_{R1} and C_{R2}, we have that for the activation energy [12], E_a;

$$ln\left[\frac{C_{R2}}{C_{R1}}\right] = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \ (10)$$

Also, for the heat of adsorption, Q_{ads} (kJ/mol)

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_2 \times T_1}{T_2 - T_1} \ (11)$$

where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2, respectively. R $(8.314kJ/mol.K)$ is the gas constant and T (K) is temperature.

The inhibition efficiency was optimized using RSM of Design Expert Software 11. Central Composite Design (CCD) (Face Centered) of the RSM was used to design the experiment for the weight loss method. Inhibitor concentration, temperature and time were the factors considered in this study. The design matrix for the experiment is shown in Table 1. The RSM was used to analyze the responses. The ANOVA and graphical analyses of the inhibition efficiency were carried out. The mathematical models in terms of coded factors were obtained. The models in terms of coded factors were used to make predictions about the response for given levels of each factor. Optimum inhibition parameters were also obtained.

Furthermore, the optimization of the inhibition efficiency was done using the central composite design of the design expert software.

Table 1: Design matrix for corrosion inhibition of Aluminium in 0.5M HCl Medium using central composite design of Design Expert 11

		Factor 1	Factor 2	Factor 3
Std	Run	A:Temperature (K)	B:Inhibitor Conc. (g/l)	C:Time (hr)
7	1	303	1	5
3	2	303	1	1
8	3	343	1	5
5	4	303	0.2	5
10	5	343	0.6	3
20	6	323	0.6	3
17	7	323	0.6	3
4	8	343	1	1
9	9	303	0.6	3
18	10	323	0.6	3
2	11	343	0.2	1
11	12	323	0.2	3
12	13	323	1	3
6	14	343	0.2	5
19	15	323	0.6	3
14	16	323	0.6	5
15	17	323	0.6	3
16	18	323	0.6	3
13	19	323	0.6	1
1	20	303	0.2	1

RESULTS AND DISCUSSION

Gravimetric (weight loss)

The weight loss analysis conducted involves: one factor at a time experiment and the response surface methodology. The results obtained are shown in Table 2 through Table 10 considering the effect of experimental parameters (concentration, temperature, and time) on the corrosion rate and the inhibition efficiency of aluminum in 0.5M HCl.

Table 2: Values of weight loss, corrosion rate, inhibition efficiency and surface coverage after 1hr

Tem. (K)	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
303	0.0	0.16	17.78		
	0.2	0.12	13.33	25.00	0.2500
	0.4	0.09	10.00	43.75	0.4375
	0.6	0.06	6.667	62.50	0.6250
	0.8	0.05	5.556	68.75	0.6875
	1.0	0.05	5.556	68.75	0.6875
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
313	0.0	0.24	26.67		
	0.2	0.13	14.44	45.83	0.4583
	0.4	0.10	11.11	58.33	0.5833
	0.6	0.06	6.667	75.00	0.7500
	0.8	0.05	5.556	79.17	0.7917
	1.0	0.04	4.444	83.33	0.8333
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
323	0.0	0.25	27.78		
	0.2	0.12	13.33	52.00	0.5200
	0.4	0.09	10.00	64.00	0.6400
	0.6	0.06	6.667	76.00	0.7600
	0.8	0.05	5.556	80.00	0.8000
	1.0	0.05	5.556	80.00	0.8000
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
333	0.0	0.27	30.00		
	0.2	0.15	16.67	44.44	0.4444
	0.4	0.14	15.56	48.15	0.4815
	0.6	0.08	8.889	70.37	0.7037
	0.8	0.08	8.889	70.37	0.7037
	1.0	0.07	7.778	74.07	0.7407
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
343	0.0	0.30	33.33		
	0.2	0.21	23.33	30.00	0.3000
	0.4	0.14	15.56	53.33	0.5333
	0.6	0.13	14.44	56.67	0.5667
	0.8	0.11	12.22	63.33	0.6333
	1.0	0.11	12.22	63.33	0.6333

Table 3: Values of weight loss, corrosion rate, inhibition efficiency and surface coverage after 2hrs

Temp. (K)	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
303	0.0	0.29	16.11		
	0.2	0.14	7.778	51.72	0.5172
	0.4	0.10	5.556	65.52	0.6552
	0.6	0.07	3.889	75.86	0.7586
	0.8	0.06	3.333	79.31	0.7931
	1.0	0.06	3.333	79.31	0.7931
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
313	0.0	0.30	16.67		
	0.2	0.15	8.333	50.00	0.5000
	0.4	0.11	6.111	63.33	0.6333
	0.6	0.07	3.889	76.67	0.7667
	0.8	0.06	3.333	80.00	0.8000
	1.0	0.05	2.778	83.33	0.8333
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
323	0.0	0.35	19.44		
	0.2	0.16	8.889	54.29	0.5429
	0.4	0.12	6.667	65.71	0.6571
	0.6	0.08	4.444	77.14	0.7714
	0.8	0.07	3.889	80	0.8000
	1.0	0.06	3.333	82.86	0.8286
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
333	0.0	0.37	20.56		
	0.2	0.19	10.56	48.65	0.4865
	0.4	0.15	8.333	59.46	0.5946
	0.6	0.10	5.556	72.97	0.7297
	0.8	0.10	5.556	72.97	0.7297
	1.0	0.09	5.000	75.68	0.7568
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
343	0.0	0.40	22.22		
	0.2	0.23	12.78	42.50	0.4250
	0.4	0.21	11.67	47.50	0.4750
	0.6	0.16	8.889	60.00	0.6000
	0.8	0.14	7.778	65.00	0.6500
	1.0	0.12	6.667	70.00	0.7000

Table 4: Values of weight loss, corrosion rate, inhibition efficiency and surface coverage after 3hrs

Temp. (K)	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
303	0.0	0.32	11.85		
	0.2	0.15	5.556	53.13	0.5313
	0.4	0.11	4.074	65.63	0.6563
	0.6	0.09	3.333	71.88	0.7188
	0.8	0.08	2.963	75.00	0.7500
	1.0	0.07	2.593	78.13	0.7813
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
313	0.0	0.34	12.59		
	0.2	0.17	6.296	50.00	0.5000
	0.4	0.13	4.815	61.76	0.6176
	0.6	0.09	3.333	73.53	0.7353
	0.8	0.07	2.593	79.41	0.7941
	1.0	0.06	2.222	82.35	0.8235
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
323	0.0	0.38	14.07		
	0.2	0.18	6.667	52.63	0.5263
	0.4	0.16	5.926	57.89	0.5789
	0.6	0.08	2.963	78.95	0.7895
	0.8	0.08	2.963	78.95	0.7895
	1.0	0.07	2.593	81.58	0.8158
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
333	0.0	0.40	14.81		
	0.2	0.25	9.259	37.50	0.3750
	0.4	0.19	7.037	52.50	0.5250
	0.6	0.17	6.296	57.50	0.5750
	0.8	0.12	4.444	70.00	0.7000
	1.0	0.11	4.074	72.50	0.7250
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
343	0.0	0.42	15.56		
	0.2	0.28	10.37	33.33	0.3333
	0.4	0.24	8.889	42.86	0.4286
	0.6	0.17	6.296	59.52	0.5952
	0.8	0.15	5.556	64.29	0.6429
	1.0	0.13	4.815	69.05	0.6905

Table 5: Values of weight loss, corrosion rate, inhibition efficiency and surface coverage after 4hrs

Temp. (K)	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
303	0.0	0.33	9.167		
	0.2	0.17	4.722	48.48	0.4848
	0.4	0.12	3.333	63.64	0.6364
	0.6	0.10	2.778	69.70	0.6970
	0.8	0.08	2.222	75.76	0.7576
	1.0	0.08	2.222	75.76	0.7576
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
313	0.0	0.36	10.00		
	0.2	0.20	5.556	44.44	0.4444
	0.4	0.15	4.167	58.33	0.5833
	0.6	0.11	3.056	69.44	0.6944
	0.8	0.08	2.222	77.78	0.7778
	1.0	0.07	1.944	80.56	0.8056
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
323	0.0	0.39	10.83		
	0.2	0.23	6.389	41.03	0.4103
	0.4	0.18	5.000	53.85	0.5385
	0.6	0.09	2.500	76.92	0.7692
	0.8	0.09	2.500	76.92	0.7692
	1.0	0.09	2.500	76.92	0.7692
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
333	0.0	0.41	11.39		
	0.2	0.27	7.500	34.15	0.3415
	0.4	0.22	6.111	46.34	0.4634
	0.6	0.19	5.278	53.66	0.5366
	0.8	0.13	3.611	68.29	0.6829
	1.0	0.12	3.333	70.73	0.7073
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^{2}hr)	IE %	Surface coverage
343	0.0	0.43	11.94		
	0.2	0.29	8.056	32.56	0.3256
	0.4	0.25	6.944	41.86	0.4186
	0.6	0.22	6.111	48.84	0.4884
	0.8	0.18	5.000	58.14	0.5814
	1.0	0.14	3.889	67.44	0.6744

Table 6: Values of weight loss, corrosion rate, inhibition efficiency and surface coverage after 5hrs

Temp. (K)	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
303	0.0	0.34	7.556		
	0.2	0.18	4.000	47.06	0.4706
	0.4	0.13	2.889	61.76	0.6176
	0.6	0.11	2.444	67.65	0.6765
	0.8	0.10	2.222	70.59	0.7059
	1.0	0.09	2.000	73.53	0.7353
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
313	0.0	0.37	8.222		
	0.2	0.21	4.667	43.24	0.4324
	0.4	0.16	3.556	56.76	0.5676
	0.6	0.12	2.667	67.57	0.6757
	0.8	0.11	2.444	70.27	0.7027
	1.0	0.11	2.444	70.27	0.7027
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
323	0.0	0.40	8.889		
	0.2	0.24	5.333	40.00	0.4000
	0.4	0.19	4.222	52.50	0.5250
	0.6	0.11	2.444	72.50	0.7250
	0.8	0.10	2.222	75.00	0.7500
	1.0	0.09	2.000	77.50	0.7750
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
333	0.0	0.42	9.333		
	0.2	0.28	6.222	33.33	0.3333
	0.4	0.23	5.111	45.24	0.4524
	0.6	0.20	4.444	52.38	0.5238
	0.8	0.14	3.111	66.67	0.6667
	1.0	0.14	3.111	66.67	0.6667
	Conc. of inhibitor (g/l)	Weight loss (g)	Cr (mg/cm^2hr)	IE %	Surface coverage
343	0.0	0.44	9.778		
	0.2	0.30	6.667	31.82	0.3182
	0.4	0.25	5.556	43.18	0.4318
	0.6	0.23	5.111	47.73	0.4773
	0.8	0.18	4.000	59.09	0.5909
	1.0	0.16	3.556	63.64	0.6364

Table 7: Adsorption parameters for the corrosion inhibition

Adsorption Isotherm	Temperature(K)	R^2	k_{ads}	$\Delta G_{ads}(kJ/mol)$	Property	
Langmuir	303	0.9919	0.789	-9.54		
	323	0.9852	0.836	-10.31		
	343	0.9995	0.675	-10.33		
Frumkin	303	0.6136	5.794	-14.55	$\propto$	-0.363
	323	0.0302	3.819	-14.39		0.0962
	343	0.7553	3.119	-14.70		-0.359
Temkin	303	0.9816	0.0187	-0.0936	a	-2.570
	323	0.9414	0.0220	-0.536		-2.322
	343	0.9925	0.0399	-2.27		-2.445
Flory-Huggins	303	0.9759	4.943	-14.15	x	0.1.29
	323	0.8678	3.990	-14.50		0.929
	343	0.8404	2.366	-13.91		1.19

Table 8: Activation energy and Heat of adsorption for the corrosion inhibition

Inhibitor concentration (g/l)	Surface coverage		Corrosion rate (mg/cm^2hr)		Activation Energy $Ea, (kJ/mol)$	Heat of adsorption , Q_{ads} (kJ/mol)
	θ_1	θ_2	303K	343K		
0.2	0.4508	0.3404	7.0772	12.2406	27.26	-10.03
0.4	0.6006	0.4575	5.1702	9.7240	31.42	-12.50
0.6	0.6952	0.5455	3.8222	8.1694	37.07	-13.87
0.8	0.7388	0.6197	3.2592	6.9108	37.39	-11.91
1.0	0.7510	0.6669	3.1408	6.2294	34.79	-8.85

Table 9: Response Surface Results

		Factor 1	Factor 2	Factor 3	Response 1
Std	Run	A:Temperature	B:Inhibitor Concentration	C:Time	Inhibition Efficiency
		(K)	(g/l)	(hr.)	(%)
7	1	303	1	5	73.53
3	2	303	1	1	68.75
8	3	343	1	5	63.64
5	4	303	0.2	5	47.06
10	5	343	0.6	3	59.52
20	6	323	0.6	3	78.95
17	7	323	0.6	3	78.95
4	8	343	1	1	63.33
9	9	303	0.6	3	71.88
18	10	323	0.6	3	78.95
2	11	343	0.2	1	30
11	12	323	0.2	3	52.63
12	13	323	1	3	81.58
6	14	343	0.2	5	31.82
19	15	323	0.6	3	78.95
14	16	323	0.6	5	72.5
15	17	323	0.6	3	78.95
16	18	323	0.6	3	78.95
13	19	323	0.6	1	76
1	20	303	0.2	1	25

Table 10: Model Summary Statistics

Source	**Std. Dev.**	**R^2**	**Adjusted R^2**	**Predicted R^2**	**PRESS**	
Linear	14.31	0.4703	0.3709	0.0408	5932.77	
2FI	15.57	0.4903	0.2550	-2.8047	23533.04	
Quadratic	**3.19**	**0.9835**	**0.9687**	**0.7942**	**1272.95**	**Suggested**
Cubic	0.3334	0.9999	0.9997	0.8675	819.43	Aliased

Table 11: ANOVA for Quadratic model of response surface methodology for the inhibition process

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	6083.50	9	675.94	66.43	< 0.0001	significant
A-Temperature	143.72	1	143.72	14.12	0.0037	
B-Inhibitor Concentration	2700.11	1	2700.11	265.35	< 0.0001	
C-Time	64.87	1	64.87	6.38	0.0301	
AB	3.21	1	3.21	0.3158	0.5865	
AC	76.32	1	76.32	7.50	0.0209	
BC	44.13	1	44.13	4.34	0.0639	
A^2	450.59	1	450.59	44.28	< 0.0001	
B^2	357.11	1	357.11	35.09	0.0001	
C^2	49.68	1	49.68	4.88	0.0516	
Residual	101.76	10	10.18			
Lack of Fit	101.76	5	20.35			
Pure Error	0.0000	5	0.0000			
Cor Total	6185.26	19				

Table 12: Optimum parameters for the corrosion inhibition process

Inhibitor Concentration (g/l)	Temperature (K)	Time $(hr.)$	Inhibition Efficiency (%)	Measured inhibition Efficiency (%)	Percentage validation (%)
0.901	*317.521*	*3.898*	*84.763*	*86.025*	*1.26*

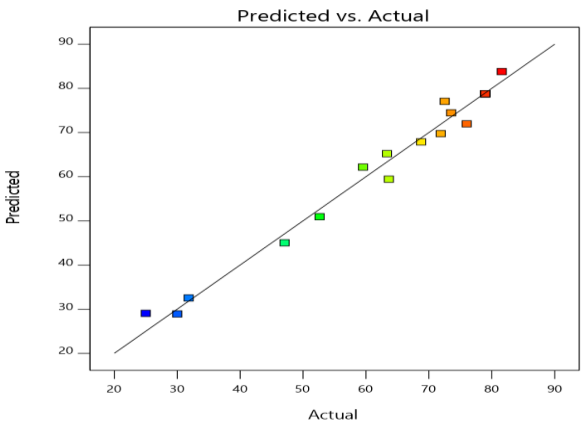

Figure 1: Graph of Actual values versus Predicted Values of the Inhibition Efficiency

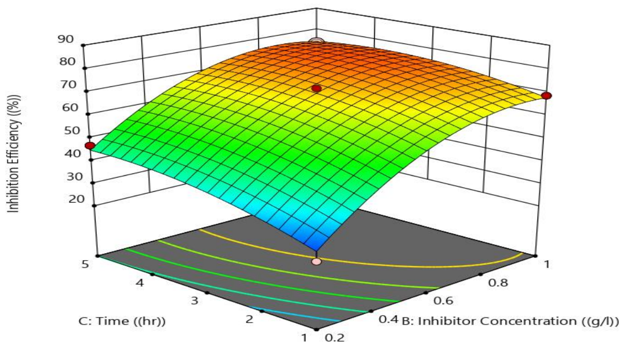

Figure 2: 3-D plot of inhibitor concentration versus temperature

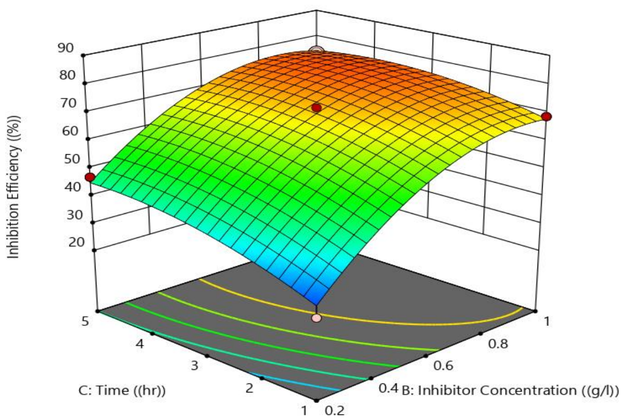

Figure.3: 3-D plot of inhibitor concentration versus time

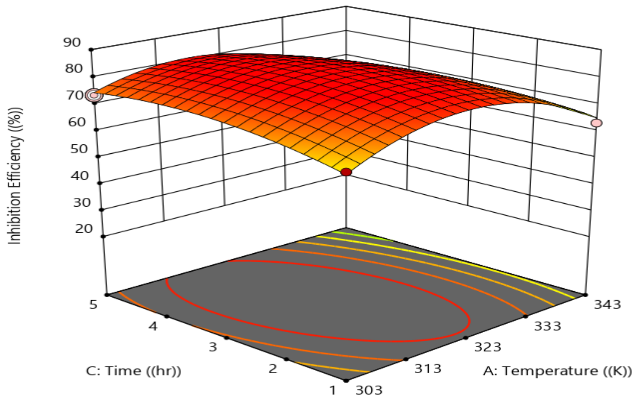

Figure 4: 3-D plot of Inhibitor Concentration versus Temperature

Weight loss (gravimetric) Method Result Analysis

Effect of experimental parameters on corrosion rate

Concentration effect: The results shown on Tables 2 through 6 signify that the rate of corrosion of aluminum in the acidic environment occurred rapidly in the blank solution. The results also indicate that corrosion rate decreased as inhibitor concentration increased. This is in consonance with the findings of many researchers [1, 4, 6, 7, 13 and 14]. Generally, corrosion rate decreases as the concentration of the adsorbate on the substrate surface (adsorbent) increases.

Effect of temperature: Considering the design temperature of 303K, 313K, 323K, 333K, and 343, corrosion rate increased with temperature as evident in Tables 2 through 6. Corrosion is an oxidation process and this implies that increase in temperature increases oxidation rate which in this case is the rate of corrosion [1]. The values of corrosion rate as displayed in the tables indicate that as temperature increased, corrosion rate also increased. In fact, the highest value occurred at the highest temperature of 343K. Reference [15] proposed that at higher temperatures, rapid oxidation of the iron component of the mild steel occurs. But in this present study, rapid oxidation of the iron component of the aluminum occurred.

Effect of time: Time is an important factor in corrosion studies. Tables 2 through 6 again indicate that the rate of corrosion increased linearly with time at various concentrations of the inhibitor. But, there exists a point at which time approached its global optimum. This point is said to be the critical time and the rate of corrosion is maximum at this period. After this critical period, the rate of corrosion decreased at subsequent concentrations of the inhibitor. Therefore, the reduction in corrosion rate of the specimen with time is traced to the adsorption and consequently the inhibitive effects of the neem seed extract. This is in perfect agreement with the finding of [16] on the green inhibitor.

Effect of experimental parameters on the inhibition efficiency

Effect of concentration: The results presented in the Tables 2 – 6 once again show that the inhibition efficiency of Azadirachta indica seed extract varied linearly with the inhibitor concentration. Therefore the highest inhibition efficiency of the green inhibitor occurred at the maximum concentration of the extract (1.0g/l). The inhibitor efficiency obtained at this concentration is 83.33%. This inhibition efficiency of Azadirachta indica seed extract may be attributed to the formation of a barrier film due to adsorption of inhibitor molecules on the metal surface involving interactions between pi electrons of inhibitor molecules and vacant d-orbitals of Fe surface atoms. The results are also in agreement with the findings of [17].

Effect of time: Considering the effect of time as a parameter, the efficiency of the inhibitor is seen to be more significant at the onset of the corrosion and its inhibitive effect retarded as the corrosion progressed.

Temperature effect: Tables 2 - 6 also show the inhibition efficiency of Azadirachta indica seed extract on the aluminum work piece at different concentrations of the inhibitor at 303K, 313K, 323K, and 333K, and 343K respectively. It is seen that at a fixed concentration of the inhibitor, the weight loss at 343K is in most of the instances higher than that occurring at 303K indicating that the inhibition efficiency of Azadirachta indica seed extract decreased with increase in temperature. The decrease may be due to competition between forces of adsorption and desorption. These very same competing forces of adsorption and desorption may also explain the occasional discrepancies in mass loss change observed in the tables. From Table 6, it can also be seen that optimum value of the inhibition efficiency of 83.3% was obtained at 313K. A decrease in inhibition efficiency with temperature is suggestive of physical adsorption.

Thermodynamic Analysis of the corrosion inhibition process

Adsorption parameters

Adsorption parameters for the corrosion inhibition of aluminum in HCl by Azadirachta indica seed extract are shown in Table 7. The negative values of the standard free energy of adsorption $\Delta G_{ads}\,(kJ/mol)$ ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the aluminum surface. Generally, the values of ΔG^o_{ads} around $-20kJ/mol$ or lower are consistent with physisorption, while those around $-40kJ/mol$ or higher have to do with chemisorptions (Umoren et al, 2006, Ebenso et al, 2009, Obot et al, 2009). The values of this parameter are closer to $-20kJ/mol$ indicating adherence to physical adsorption. The dimensionless parameters, R^2 (degree of determination), K (the adsorption equilibrium constant), α (lateral interaction term describing the interaction in adsorbed layer), a (the attractive parameter) and x (the size parameter, a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule) were used to measure the fitness of the isotherms. The Langmuir isotherm has the highest values of R^2 (0.9919, 0.9852, and 0.999 at 303 K, 323 K, and 343K respectively), which showed strong adherence of the inhibition process to Langmuir adsorption isotherm. The lateral interaction term α, has values (-0.363, 0.0962, and -0.359 at 303K, 323K, and 343K respectively). The positive sign suggests attractive behaviour of the inhibitor on the Al surface at temperature of 323K and a repulsive behavior of the inhibitor at temperature of 303K and 343K. The attractive parameter a, has negative values of -0.570, -2.322, and -2.445 indicating that repulsion exists in the adsorption layer. The size parameter has positive values of 0.129, 0.929, and 1.19 which show that the adsorbed species of the extract was bulky.

Activation energy and the heat of adsorption for the corrosion inhibition process

Analysis of the temperature dependence of the inhibition efficiency coupled with the activation energies elucidates the possible mechanism of adsorption. An increase in inhibition efficiency with rise in temperature, with analogous decrease in corrosion activation energy in the presence of an inhibitor compared to its absence is usually suggestive of chemisorption, while a decrease in inhibition efficiency with rise in temperature, with corresponding increase in corrosion activation energy in the presence of inhibitor compared to its absence is ascribed to physisorption [18, 19, 20, 21 and 1]. The values of activation energy as displayed in Table 8 are therefore indicative of physisorption since they increased with increase in temperature and decrease in inhibition efficiency. The negative sign of the heat of adsorption also showed that the inhibitive process was an exothermic reaction. Therefore, a spontaneous adsorption of the extract on the Al surface occurred.

Response Surface Methodology Result Analysis

Table 9 shows the response surface results of the experiment. The best model maximizing the Adjusted R^2 and the Predicted R^2 as shown in Table 10 is the quadratic model which is the suggested model for the experimental data**.** The fit statistics of the response data indicates an R^2

value of 0.9835, Adj R^2 of 0.9687 and Adeq precision of 24.5359. The predicted R^2 of 0.7965 is in reasonable agreement with the Adj R^2 of 0.9687 since the difference is less than 0.2. The Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 24.5359 obtained indicates an adequate signal. It's a sign that this model can be used to navigate the design space.

Considering general model terms, the model for the corrosion inhibition of Al in HCl by neem seed extract is expressed by Equation 12.

$$IE = 78.77 - 3.79A + 16.43B + 2.55C - 0.63AB - 3.09AC - 2.35BC - 12.80A^2 - 11.40B^2 - 4.25C^2 \quad (12)$$

The coefficients as showed in equation 12 estimate the expressed change in response per unit change in time factor value when all remaining factors are held constant. A, B, C represent the experimental factors; where A = temperature of reaction, B = inhibitor concentration and C= time, AB= effect of temperature and inhibitor concentration on the inhibition efficiency, AC= effect of temperature and time on the inhibition efficiency, and BC= effect of inhibitor concentration and time on the inhibition efficiency. The inhibition efficiency is a function of inhibitor concentration (C, g/l), temperature (T, K) and time (t, hr). The positive signs in the model signify synergistic effect, while the negative signs signify antagonistic effect. The highest power of at least one of the variables is 2, which shows that the mathematical model is a quadratic model.

Table 11 presents the analysis of variance (ANOVA), the degree of freedom (Df), Fisher test (F-test) and probability value (p-value). The model F-value of 66.43 implies the model is significant. There is only 0.01% chance that that an F-value this large could occur due to experimental noise. The p-values less than 0.0500 indicate that the model terms are significant. In this case: A, B, C, and AC. AB is the only insignificant model term. The significant model terms are shown in equation 13.

$$IE = 78.77 - 3.79A + 16.43B + 2.55C - 3.09AC - 12.80A^2 - 11.40B \quad (13)$$

Plot of predicted versus actual inhibition efficiency was used to test the significance of the model as shown in Figure 1. The predicted versus actual plot gave a linear graph which signifies consistency of the experimental response. The 3-D surface plots (Figure 2 - Figure 4) show the interactions between the designed factors with their response. The plots indicate that inhibitor concentrations have more effect on the response. Increased inhibitor concentration favors the response, but at high reaction temperature and time, inhibition efficiency of the organic inhibitor decreases.

Table 12 presents the specific optimum conditions for the defined inhibition efficiency. The goal here was to obtain maximum inhibition efficiency for the aluminum corrosion in HCl medium referred to as the global optimum. Optimum response data is given as 84.763% and this was obtained at inhibitor concentration of 0.901 g/l, temperature of 317.521 K and immersion time of 3.898 hrs. The result was validated with minor percentage deviation of +1.26. It shows that response surface methodology of Design Expert Software 11 was adequate for the optimization of the inhibition process.

CONCLUSION

The results for the weight loss method signify that the inhibitive effect of Azadirachta indica seed extract increased as the inhibitor concentration increased; with the highest inhibition efficiency recorded at the highest inhibitor concentration of 1.0g/l. The adsorption of the extract on the aluminum surface adhered to the mechanism of physical adsorption. The isotherms were perfectly fitted by Langmuir isotherm. The values of the isotherm properties showed attractive behaviour of the extract on the aluminum surface, repulsion in the adsorption layer and bulky adsorbed species of the extract. A quadratic model described the inhibition efficiency as a function of inhibitor concentration, temperature and immersion time with inhibitor concentration having a greater effect. Optimum inhibition efficiency of 84.763% was obtained at inhibitor concentration of 0.901 g/l, temperature of 317.521K and immersion time of 3.898 hrs.

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