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Modeling the Corrosion Inhibition of Mild Steel in HCl Medium with the Inhibitor of Pawpaw Leaves Extract

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Abstract

Modeling the corrosion inhibition of mild steel in HCl medium with inhibitor of pawpaw leaves extract is presented. The extract was analyzed using gas chromatography-mass spectrometry. Thermometric and gravimetric methods were employed in the corrosion inhibition study. The inhibition efficiency was modeled and optimized using response surface methodology (RSM). It was observed that the free energy of adsorption (ΔG_{ads}) was negative and less than the threshold value of -40 kJ/mol. The adsorption of the extract was spontaneous, and occurred according to the mechanism of physical adsorption. A quadratic model was generated, with optimum inhibition efficiency of 80.29% obtained. The extract was highly efficient in the corrosion control process. It is effective for surface treatment of mild steel in the acid medium. Therefore, it is recommended that pawpaw leaves extract should be employed as corrosion inhibitor in oil well acidizing and surface treatment of mild steel.

***Keywords**:* Corrosion, HCl, Mild Steel, Pawpaw Leaves.

Introduction

It has been acknowledged that mild steel is widely employed in most industries, due to its low cost and availability for the fabrication of various reaction vessels, such as cooling tower tanks and pipelines [1]. Mild steel corrodes as a result of an electrochemical reaction with its environment. To prolong the life span of mild steel structures, inhibitive additives are needed in pickling and other related maintenance operations. In view of environmental concern, efforts are geared towards applications of plant extracts as corrosion inhibitors in oil well acidizing and inhibition additives for surface treatment of metals. In the development of an eco-friendly corrosion inhibitor of plant origin, pawpaw leaves extract is of great

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interest. Pawpaw leaves produce several alkaloids and other phytochemicals with important pharmaceutical and industrial applications.

Experimental methods

Sheets of mild steel with P (0.02%), Mn (0.11%), Si (0.02%), S (0.02%), Cu (0.01%), C (0.23%), Ni (0.02), Cr (0.01%) and Fe (99.56 %) composition were cut into coupons (5 cm x 4 cm). Leaves of pawpaw (*Carica papaya*) were collected from Akpugo, Enugu State, Nigeria. In the extraction of the pawpaw leaves extract and surface preparation of the mild steel, the method used in the previous study was adopted [2]. Standard method was used for the chemical analysis of the extract [3, 4]. It was carried out using a gas chromatography-mass spectrometer (GCMS-QP2010 PLUS, SHIMADZU). An acid medium of 1.0 M HCl was used for the study.

Thermometric and gravimetric measurements were used in the corrosion inhibition study. The inhibition efficiency was optimized using response surface methodology (RSM). For the thermometric measurements, the method used by previous authors was adopted with slight modifications [5, 6]. The inhibitor efficiency was determined using Equation (1),

$$IE\% = \left(1 - \frac{RN_{add}}{RN_{free}}\right) * 100 \qquad (1)$$

where RN_{free} and RN_{add} are the reaction numbers for the metal dissolution in free and inhibited corrosive medium, respectively. The reaction number (RN) was evaluated using Equation (2),

$$RN = \frac{T_m - T_i}{t} \qquad (2)$$

where T_m and T_i are the maximum and initial temperatures (in ºC) respectively, and t is the time in minutes elapsed to reach T_m.

For the gravimetric measurements, the weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE) and degree of surface coverage were determined using Equations (3), (4) and (5), respectively. The surface coverage was obtained using the following Equation (6) [7],

$$\Delta w = w_i - w_f \qquad (3)$$

$$CR = \frac{w_i - w_f}{At} \qquad (4)$$

$$IE\% = \frac{\omega_0 - \omega_1}{\omega_0} * 100 \qquad (5)$$

$$\theta = \frac{IE}{100} \qquad (6)$$

where w_i and w_f are the initial and final weight of mild steel samples, respectively; ω_1 and ω_0 are the weight loss values in presence and absence of the

inhibitor, respectively. A is the total area of the mild steel sample and t is the immersion time.
Considering the corrosion rates of the metal at T_1 and T_2 as CR_1 and CR_2, the activation energy, E_a, was obtained using Equation (7) [8-10].

$$\ln\left({CR_2}/{CR_1}\right) = \left({E_a}/{2.303R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (7)$$

The heat of adsorption Q_{ads} (kJmol^{-1}) was calculated using Equation (8) [9, 11],

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] * \frac{T_2 \cdot T_1}{T_2 - T_1} \quad (8)$$

where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2, respectively.
Different adsorption isotherms were used to determine the adsorption mechanism of the extract on the metal surface. Langmuir, Frumkin, Temkin and Flory-Huggins isotherms are shown in Equations (9), (10), (11) and (12), respectively [9, 12, 13, 14].

$$log\frac{C}{\theta} = \log C - logK \quad (9)$$

$$\log\left((C) * \left(\frac{\theta}{1-\theta}\right)\right) = 2.303logK + 2\alpha\theta \quad (10)$$

$$\theta = -\frac{2.303logK}{2a} - \frac{2.303\, logC}{2a} \quad (11)$$

$$\log\left(\frac{\theta}{C}\right) = \log K + xlog(1-\theta) \quad (12)$$

where C is the concentration of the inhibitor, K is the adsorption equilibrium constant, θ is the degree of surface coverage, α is the lateral interaction term describing the interaction in adsorbed layer, a is the attractive parameter, and x is the size parameter and a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.
The free energy of adsorption (ΔG_{ads}) was calculated according to Equation (13) [9, 12].

$$\Delta G_{ads} = -2.303RTlog(55.5K) \quad (13)$$

where R is the gas constant, and T is the temperature.

Results and discussions

Analysis of the pawpaw leaves extract

In Fig. 1, the GC MS chromatogram of the pawpaw leaves extract shows various peak levels. Each of the peaks represents compounds, as determined by the GC MS. The analysis revealed the presence of C_8H_7N (117g/mole: Benzyl nitrile; Benzyl cyanide; Benzene acetonitrile; Phenylacetonitrile; Phenyl acetyl nitride);

$C_9H_9NO_3$ (179 g/mole (Benzene propanoic acid); C_8H_7N (117 g/mole: 2,4,6-Cycloheptatriene-1-carbonitrile; 1,3,5-Cycloheptatriene-7-carbonitrile; 7-Cyano-1,3,5-cycloheptatriene; 7-Cyanocycloheptatriene; 1-Cyano-2,4,6-cycloheptatriene; 7-cyanotropilidene); $C_8H_8O_2$ (136 g/mole: Benzaldehyde, 2-Hydroxy-4-methylbenzaldehyde). It also contains $C_5H_{10}N_2O_3$ (146 g/mole: Levoglutamide; l-Glutamine; Glutamic acid amide) $C_7H_{14}O_6$ (194 g/mole: Methyl beta.-d-galactopyranoside); $C_{16}H_{30}O$ (238 g/mole: cis-9-Hexadecenal; 9-Hexadecenal); $C_{14}H_{26}O$ (210 g/mole 9-Tetradecenal); $C_{18}H_{34}O_2$ (282 g/mole: Oleic Acid, 9-Octadecenoic acid; cis-9-Octadecenoic Acid; cis-.delta.9-Octadecenoate); $C_{16}H_{30}O_2$ (254 g/mole: 9-Hexadecenoic acid) and $C_{22}H_{42}O_2$ (338 g/mole: Erucic acid, 13-Docosenoic acid). The extract contains organic compounds with polar atoms capable of being adsorbed onto the metal surface through the polar atoms [15].

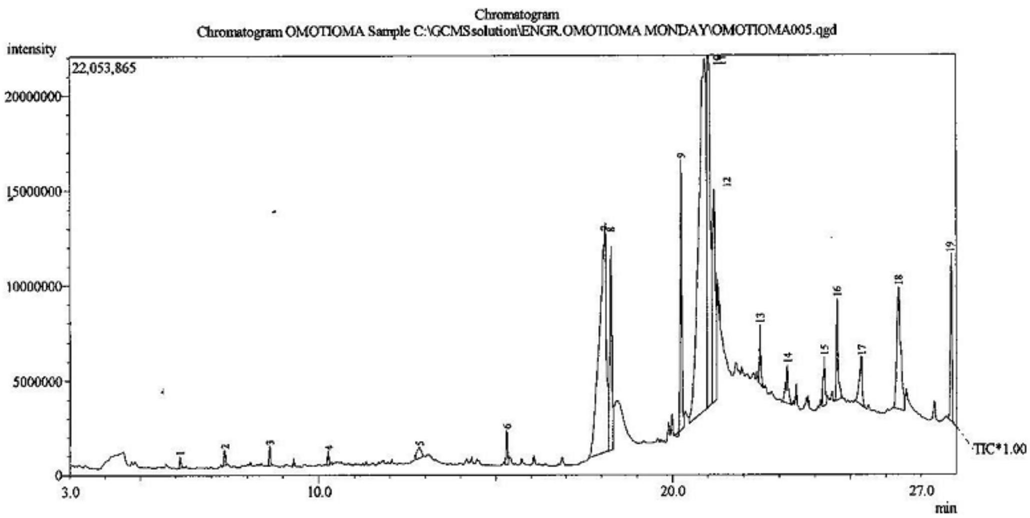

Figure 1. The GC MS chromatogram of the pawpaw leaves extract.

Results from the thermometric method

Effects of the inhibitor's concentration on the reaction number (RN) and the inhibition efficiency (IE) are shown in Table 1. Increase in concentration lowers the reaction number, but increases the inhibition efficiency of the inhibitor. It agrees with previous observations [2, 5].

Table 1. Effects of concentration of the extract on the RN and IE (%).

Medium	Inh. conc., g/L	pawpaw leaves extract	
		RN	IE (%)
HCl	0.0	0.0327	
	0.2	0.0164	49.9
	0.4	0.0116	64.48
	0.6	0.0074	77.38
	0.8	0.0057	82.49
	1.0	0.0048	85.24

Results from the Gravimetric Method

In Table 2, corrosion rate decreases with an increase in the extract concentration. Highest inhibition efficiency of 83.00% was obtained. It showed that pawpaw leaves extract can be used as an additive for pickling, cleaning and descaling operations. The extract is efficient for corrosion control of mild steel in acid medium.

Table 2. Data of corrosion inhibition of mild steel in HCl with pawpaw leaves extract.

Time (hr)	Parameter	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L	1.0 g/L	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L	1.0 g/L
		303 K					333 K				
8	Weight loss (g)	0.037	0.03	0.02	0.023	0.017	0.057	0.05	0.04	0.037	0.037
16		0.057	0.04	0.027	0.02	0.017	0.097	0.07	0.06	0.057	0.053
24		0.077	0.057	0.033	0.030	0.027	0.13	0.093	0.080	0.077	0.070
8	CR (mg/cm^2hr)	0.231	0.188	0.125	0.144	0.106	0.356	0.313	0.25	0.231	0.231
16		0.178	0.125	0.084	0.062	0.053	0.303	0.219	0.187	0.178	0.166
24		0.160	0.119	0.069	0.063	0.056	0.271	0.194	0.167	0.160	0.146
8	IE (%)	35.09	47.37	64.91	59.65	70.18	25.97	35.06	48.05	51.95	51.95
16		43.00	60.00	73.00	80.00	83.00	30.71	50.00	57.14	59.29	62.14
24		43.80	58.39	75.91	78.10	80.29	35.00	53.50	60.00	61.50	65.00

Energy activation and adsorption heat process

In Table 3, the values of the activation energy and heat of adsorption indicate that the adsorption of the pawpaw extract on the surfaces of mild steel has been conformed with the mechanism of physical adsorption and exothermic reaction.

Table 3. Activation energy and heat of adsorption for the corrosion inhibition process.

Medium	Conc. of the plant extract (g/L)	Activation energy (kJ/mol)	Heat of adsorption, Q_{ads} (kJ/mol)
HCl	0.2	33.934	-10.341
	0.4	31.473	-5.554
	0.6	56.920	-20.760
	0.8	60.021	-22.461
	1.0	61.709	-21.968

Adsorption parameters

The parameters of Langmuir, Frumkin, Temkin and Flory-Huggins isotherms are presented in Table 4. Considering the fitted data to Langmuir isotherm, R^2 values are very close to unity, indicating strong adherence to Langmuir adsorption isotherm [10, 16]. The application of Langmuir isotherm to the adsorption of the extract indicates that there is no interaction between adsorbate and adsorbent. The lateral interaction term (α) gave positive values, suggesting attractive behaviour of the inhibitor on the mild steel surface. The attractive parameter values (a) were negative, indicating that repulsion in the adsorption layer exists [10]. The values of the size parameter (x) were positive. They show that the adsorbed species of the extract were bulky [9]. The values of ΔG_{ads} were negative and lower than the threshold value of -40 kJ/mol required for chemical adsorption. It showed that adsorption of the extract on the metal surface followed the mechanism of physical adsorption [9, 17].

Table 4. Adsorption parameters for the corrosion inhibition process.

Adsorption isotherm	Temperature (K)	R^2	K	ΔG_{ads} (kJ/mol)	Property	
Langmuir isotherm	303	0.9798	0.8513	-9.7		
	333	0.968	0.6874	-10.1		
Frumkin isotherm	303	0.9886	0.0893	-4.0	α	1.8377
	333	0.9833	0.0892	-4.4		2.0206
Temkim isotherm	303	0.958	30.849	-18.8	a	-2.064
	333	0.949	38.814	-21.3		-2.735
Flory-Huggins isotherm	303	0.897	3.3189	-13.1	x	0.805
	333	0.894	3.7584	-14.8		1.371

Results as analyzed by RSM

Table 5 showed the dependency of weight loss, corrosion rate and inhibition efficiency on concentration, temperature and time. Optimum inhibition efficiency of 80.29% was obtained.

Table 5. RSM result of the corrosion inhibition of mild steel in HCl medium.

Std	Run	Factor 1; A: Inhibitor conc.(g/L)	Factor 2; B: Temperature (K)	Factor 3; C: Time (h)	Response 1; Weight loss (g)	Response 2; Corrosion rate (mg/cm^2h)	Response 3; Inhibition efficiency (%)
1	1	0.2	303	8	0.037	0.231	35.09
15	2	0.6	318	16	0.047	0.147	58.41
10	3	1	318	16	0.04	0.125	64.6
9	4	0.2	318	16	0.07	0.219	38.05
19	5	0.6	318	16	0.047	0.147	58.41
18	6	0.6	318	16	0.047	0.147	58.41
3	7	0.2	333	8	0.057	0.356	25.97
4	8	1	333	8	0.037	0.231	51.95
6	9	1	303	24	0.027	0.056	80.29
7	10	0.2	333	24	0.13	0.271	35
13	11	0.6	318	8	0.037	0.231	44.78
8	12	1	333	24	0.07	0.146	65
5	13	0.2	303	24	0.077	0.16	43.8
20	14	0.6	318	16	0.047	0.147	58.41
17	15	0.6	318	16	0.047	0.147	58.41
16	16	0.6	318	16	0.047	0.147	58.41
12	17	0.6	333	16	0.057	0.209	52.14
14	18	0.6	318	24	0.047	0.098	67.13
2	19	1	303	8	0.017	0.106	70.18
11	20	0.6	303	16	0.04	0.125	60

The statistical analysis of the data is shown in Table 6. In graphical form, predicted versus actual values of the inhibition efficiency were highly correlated (Fig. 2). The general model with combined significant and insignificant terms is presented in Equation (14). The quadratic model relates the inhibition efficiency (IE) with concentration (A), temperature (B) and time (C). Considering only the significant terms, the model is reduced to Equation (15). From the statistical analysis, there was only a 0.01% chance that large F-value could occur due to noise. The source of noise may be attributed to non-controllable factors of oxygen content and flow rates of the inhibitors' functional groups. The models are significant and can be used to navigate the design space.

Table 6. ANOVA for the corrosion inhibition of mild steel in HCl by pawpaw leaves extract.

ANOVA for Response Surface Quadratic model						
Analysis of variance table [partial sum of squares - Type III]						
Source	**Sum of Squares**	**Df**	**Mean Square**	**F Value**	**p-value Prob> F**	
Model	3376.36	9	375.15	41.94	< 0.0001	Significant
A-Inhibitor conc.	2374.99	1	2374.99	265.53	< 0.0001	
B-Temperature	351.65	1	351.65	39.32	< 0.0001	
C-Time	400.06	1	400.06	44.73	< 0.0001	
AB	30.42	1	30.42	3.40	0.0949	
AC	3.67	1	3.67	0.41	0.5361	
BC	1.33	1	1.33	0.15	0.7080	
A^2	82.95	1	82.95	9.27	0.0123	
B^2	1.54	1	1.54	0.17	0.6874	
C^2	2.04	1	2.04	0.23	0.6428	
Residual	89.44	10	8.94			
Lack of fit	89.44	5	17.89			
Pure error	0.000	5	0.000			
Cor total	3465.80	19				
Std. dev.	2.99		R-Squared			0.9742
Mean	54.22		Adj R-Squared			0.9510
C.V. %	5.52		Pred R-Squared			0.8045
PRESS	677.66		Adeq Precision			26.165

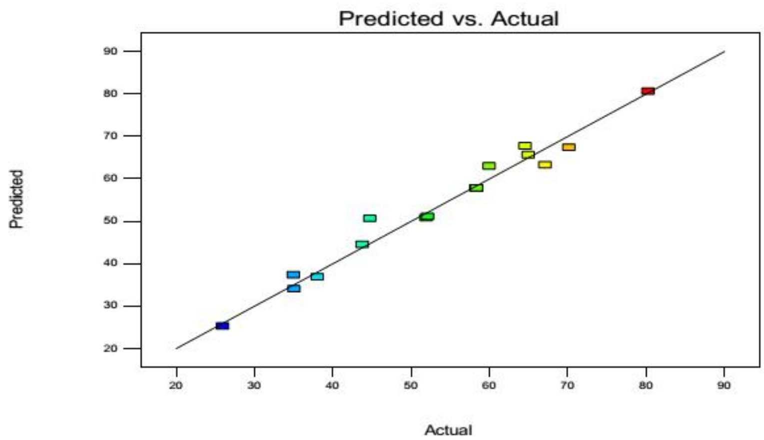

Figure 2. Predicted versus actual IE (%).

$$IE = +57.77 + 15.41*A - 5.93*B + 6.32*C - 1.95*A*B + 0.68*A*C + 0.41*B*C - 5.49*A^2 - 0.75*B^2 - 0.86*C^2 \quad (14)$$

$$IE = + 57.77 + 15.41*A - 5.93*B + 6.32*C - 5.49*A^2 \quad (15)$$

Conclusion

A quadratic model was generated, with high inhibition efficiency of 80.29% obtained. The extract is effective for surface treatment of mild steel in acid medium. It is therefore recommended that pawpaw leaves extract should be employed as corrosion inhibitor in oil well acidizing and other related surface treatment of mild steel.

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