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Corrosion Control of Aluminum Alloy in HCl Medium Using Extract of *Ocimum gratissimum* as Inhibitor

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ABSTRACT

The corrosion control of aluminum alloy in HCl medium using Ocimum gratissimum (OG) leaves extract was investigated. Thermometric, gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopic techniques were employed in the corrosion control study. The leaves extract of Ocimum gratissimum was characterized by Fourier Transform Infrared (FTIR) spectroscopy and Gas Chromatography-Mass Spectroscopy (GC-MS). The FTIR spectrophotometer was also used to analyze the corrosion product for the identification of the functional groups responsible for the corrosion control process. The corroded aluminum alloy was studied using Scanning Electron Microscopy (SEM). It was observed that stretched N-O, C-H, S-S, C=O, N-H, C-Cl, C-O, O-H were the predominant functional groups responsible for the corrosion inhibition process. There was a synergy among the functional groups and molecular compounds of the extract in the corrosion inhibition process. Quadratic model was adequate for the description of the Inhibition Efficiency (IE) as a function of the considered factors of the inhibition process. Optimum IE of 80.09% at acid concentration of 1.1 M, inhibitor concentration of 1.3 gm/l, temperature of 312 K and time of 6 h was obtained. The plant extract was identified as mixed-type inhibitor that can control both the anodic and cathodic corrosion.

Keywords: *Ocimum gratissimum*, Corrosion control, Aluminum alloy, Inhibitor

INTRODUCTION

Aluminum and its alloy are very attractive materials for engineering applications due to their low cost, high thermal and electrical conductivity, light weight and mechanical strength [1]. After iron, aluminum is the second most widely used metal in the world [2]. Aluminium and its alloy are readily attacked by fuel methanol. A 2% H_2O in methanol and 5% H_2O and 15 mg ethanoic acid in ethanol have been found to cause severe corrosion in automotive parts [3]. Corrosion is seen as the degradation of metal as a result of its electrochemical reaction with the environment. It can also be regarded as the deterioration of a material or its properties because of the reaction with the environment [4]. It occurs when protective mechanisms have been overlooked, broken down, or have been exhausted, leaving the metal vulnerable to attack. The common approach for corrosion protection is to use only durable materials. However, this approach involves huge cost and investment. The use of inhibitors is one of the best methods of protecting metals against corrosion at a relatively low cost [5]. An inhibitor can be chosen from compounds that contains heteroatom in their aromatic ring system or synthesized from cheap raw material [6]. The known hazardous effects of most synthetic corrosion inhibitors led to research into the use of some natural products.

The recent trend is towards environmentally friendly inhibitor [7]. Most of the natural products are no-toxic, cheap, biodegradable and readily available in abundance [8]. The protective efficiency is based on the adsorption ability of their molecule, where the resulting adsorbed film acts as a barrier separating the metal from the corroding medium. According to Oguzie [9], the inhibitor acts as the inter phase created by corrosion product between the metal and aqueous corroding metal. Thus, the nature of the inhibitor interaction with the metal and efficiency may be dependent on the chemical, mechanical and structural characteristic of this adsorbed film layer [9]. The extent of inhibition depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor and the type of corrosion media [10-12]. Several works has been reported with an effort to use-natural products like plant leaves or plant extracts as corrosion inhibitors. Research has shown that plant such as the seeds and leaves of *Azadirachta indica* [13], extract of *Musa acuminata* peel [14], aqueous extract of *Vernonia amygdalina* [15], extract of *Telfriria occientalis* [16], *Gmelina arborea* bark extract [17], ethanol extract of leaves of castor oil [18] and acid extract of *Opunta* [19] have been used to inhibit the corrosion of metals in acidic and alkaline solutions. Green corrosion inhibitors are biodegradable and do not contain heavy metals or toxic compounds [20]. Oganniran [21] studied the antibacterial effects of the leaves extract of *Ocimum gratissimum* and *Piper guineense* on *Escherichia coli* and *Staphylococcus aureus.*

The inhibitor under investigation is *O. gratissimum* leaves extract. *O. gratissimum* is called "Nchanwu" in Igbo language. It belongs to the family of Lamiaceae. It is also used as food vegetable. In medicine *O. gratissimum* leaves extract is used to treat skin infection, bronchitis and conjunctivitis [21]. *O. gratissimum* leaves are rich in heterocyclic compounds of high molecular weight with atoms like oxygen, sulphur, the halogens and nitrogen incorporated in their molecular structures. There is need to study and optimize the Inhibition Efficiency (IE) of *O. gratissimum* leaves extract as corrosion inhibitor. The aim of this work is to study the extract of *O. gratissimum* as corrosion inhibitor of aluminum alloy in HCl medium.

MATERIALS AND METHODS

All the chemicals used for this study are of analytical grade. 0.4 M, 0.75 M, and 1.10 M HCl (36% pure, specific gravity of 1.18) were used as the acid media, while ethanol was used for the extraction of the plant extract.

Extraction of the plant extract

Leaves of *O. gratissimum* plant were obtained from Ariaria main market located in Aba Metropolis, Enyimba city, Abia state, Nigeria. The leaves were washed with distilled water and sun-dried for 8 days. The dried leaves were ground with an electric grinder (Lexus type) so as to increase the surface area. 30 g of the ground plant leaves was measured and soaked in 1000 ml of ethanol for about 48 h. At the end of 48 h, the plant leaves mixture was filtered using Whatman no. 2 filter paper of 155 mm size. The filtrate obtained is a mixture of ethanol and plant extract. The extract contained in ethanol solvent was concentrated by distilling off the solvent (Evaporated to dryness). The plant extract was stored for the corrosion inhibition study.

Metals preparation

Aluminum alloy sheets with weight percentage composition: Cu (0.04%), Mn (0.008%), Si (0.0004%), Zn (0.005%), Pb (0.002%), Fe (0.003%), Al (99.94%) was obtained from Innoson Aluminum Nig. Ltd Aba, Enyimba City, Nigeria. The aluminum sheets were mechanically pressed cut into different coupons size of dimension 3 × 3 × 0.1 cm. Each coupon was sand papered, polished and perforated at one end by mechanical punching. Each coupon was degreased by washing with ethanol, rinsed with acetone and allowed to dry in air before preserving in desiccators to avoid contact with moisture. The initial weight of the coupon was recorded by electronic weighing machine.

FTIR analysis of the extract and corrosion product

The Aluminum alloy was immersed in the HCl medium for 18 h in the presence of the *O. gratissimum* leaves Extract. At the end of the corrosion study, the corrosion product was collected with the aid of sample bottle. Fourier Transform Infrared (FTIR) spectrophotometer (Shimadzu, Model: 1R Affinity 1:S/N A 2137470136 Si) was used to analysis the pure extract and corrosion product. The functional group of the leaves extract and that of the corrosion product were determined.

Gas chromatography-mass spectrometer (GC-MS) analysis *O. gratissimum* leaves extract

GC-MS, Model: QP 2010 Plus Shimadzu Japan was used to analyze the chemical composition of the extract. The identification of compounds was accomplished by comparison of Retention Time (RT) and fragmentation pattern, as well as the mass spectra of the GC-MS.

Scanning electron microscope (SEM) analysis

Samples of aluminum alloy coupons were immersed in HCl medium in the absence and presence of *O. gratissimum* leaves extract. SEM was used to study the surface morphologies of the samples in the inhibited and uninhibited HCl media.

Corrosion control study

Thermometric method of the corrosion control study

The aluminum samples were immersed in beakers containing inhibited and uninhibited HCl medium. The beakers were placed in thermostat set at 30°C. The progress of the corrosion reaction was monitored and the temperature of the system containing the aluminum alloy and the test solution were recorded until a steady temperature value was obtained. This method enabled the computation of the Reaction Number (RN) using Equation 1 [14,18].

$$\mathrm{RN}=\frac{\mathrm{Tm}-\mathrm{T\iota}}{\mathrm{t}}\ (°\mathrm{C/min.}) \qquad (1)$$

Where, T_m is the maximum temperature attained by the system, T_i is the initial temperature and t is the time. The IE (IE%) of the inhibitor used was calculated using Equation 2 [18].

$$\mathrm{IE\%}=\frac{\mathrm{RNo}-\mathrm{RNi}}{\mathrm{RNo}}\times\frac{100}{1} \qquad (2)$$

Where, R_{No} is the reaction number of the aqueous acid in the absence of the inhibitor (*O. gratissimum*) and R_{Ni} is the reaction number of the aqueous acid in the presence of the inhibitor (*O. gratissimum*).

Potentiodynamic polarization method of corrosion control study

Electrochemical analysis was conducted using an instrument known as Potentiostat/Galvanostat 263 electrochemical system workstation comprising of a conventional three electrode corrosion cell. A graphite rod and a saturated calomel electrode were used as counter and reference electrodes respectively. Aluminum alloy specimen was fixed in epoxy resin with its surface area up to 1 cm^2 exposed to the test solution, and served as the working electrodes. The electrochemical behaviour of aluminum alloy sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were carried out in the 1.10 M HCl and 0.75 M HCl containing different concentrations of the inhibitor (0.1 gm/l and 1.3 gm/l) by changing the electrode potential (E_{corr}) automatically from -250 to +250 mV *vs.* corrosion potential (C_{corr}) at a scan rate of 0.33 mVs^{-1}. The linear Tafel segment of the anodic and cathodic curve was extrapolated to corrosion potential to obtain the corrosion current densities (ι_{corr}) [22]. The IE was determined using Equation 3:

$$\text{IE\%}=\left(\frac{i_o\,corr - i\,corr}{i_o\,corr}\right) \times \frac{100}{1} \quad (3)$$

Where, i_{ocorr} is the uninhibited current density ι_{corr} is the inhibited current density.

Electrochemical tests

The electrochemical impedance spectroscopy (EIS) measurement was carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Antolab 1.7 computer at E_{corr} after immersion in solution without bubbling. After the determination of steady-state, current at a corrosion potential (E_{corr}), sine wave voltage (10 mV) peak to peak, at a frequencies between 100 kHz and 10 MHz was superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 h of experiment at 298 K. The impedance diagrams were given in the Nyquist representation. The experiments were repeated several times to ensure the reproducibility [23].

Weight loss (gravimetric) method using one factor at a time

In one factor at a time method of weight loss analysis, the weight loss was carried out with aluminum alloy at different temperatures, various concentrations of *O. gratissimum* and various concentrations of HCl. According to this method, aluminum alloy coupons of dimension 3 × 3 × 0.1 cm each were initially weighed, and the weight recorded using a Gulfex electronic machine. The weighed coupons were separately immersed in 250 ml open beakers of HCl in the absence and presence of various concentrations of the inhibitor. At regular time interval, the immersed aluminum alloy coupons were taken out and washed in acetone and scrubbed with brittle brush under running water, dried and reweighed. The weight loss (Δw), corrosion rate (CR), and the IE were determined in each case using Equations 4-6, respectively.

$$\Delta w=W_1 - W_2 \quad (4)$$

$$\text{CR}=\frac{W1-W2}{Ac*t} \quad (5)$$

$$\text{IE\%}=\frac{Wo-Wi}{Wo}*\frac{100}{1} \quad (6)$$

And, the degree of surface coverage θ is given by Equation 7 [15]:

$$\theta=\frac{Wo-Wi}{Wo} \quad (7)$$

Where, W_1 and W_2 are the initial and final weight of aluminum alloy samples respectively. W_o and W_i are weight loss without inhibitor and weight loss with inhibitor respectively. A_c is the total cross sectional area of the aluminum alloy and t is the time of immersion.

Thermodynamic parameters

Considering the corrosion rates of the materials at T_1 and T_2 as CR_1 and CR_2, Arrhenius law (Equation 8) was used to determine the activation energy [15,24]. The heat of adsorption Q_{ads} (kJ/mol^{-1}) was calculated using Equation 9 [15].

$$\text{Log}\left({}^{CR_2}\!/_{CR_1}\right) = \left({}^{E_a}\!/_{2.303R}\right)\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \quad (8)$$

$$Q_{ads}=2.303\text{ R }[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)] \times \left(\frac{T_2 \times T_1}{T_2 - T_1}\right) \quad (9)$$

Where, A is the pre-exponential factors, E_a is the activation energy of the reaction, R is the universal gas constant, θ_1 and θ_2 are the degrees of surface coverage at temperatures of T_1 and T_2 respectively.

Adsorption isotherms

The experimental data obtained for the degree of surface coverage were used to test for the applicability of different adsorption isotherms. The data were fitted into Langmuir, Frumkin, Temkin and Flory-Huggins isotherms of Equations 10-13, respectively [15,18]:

$$log\ \frac{C}{\theta} = log\ \text{C - Log K} \quad (10)$$

$$log\ [(C) \times (\frac{\theta}{1-\theta})]=2.303 \log K+2a\theta) \quad (11)$$

$$\Theta = \frac{2.303 \log K}{2\propto} - \frac{2.3030\ log\ C}{2\propto} \quad (12)$$

$$\text{Log } [\frac{\theta}{C}]=\log K+x \log (1–\theta) \quad (13)$$

Where, C is the concentration of the inhibitor, K is the adsorption equilibrium constant and θ is the degree of surface coverage, ‘a’ is the lateral interaction term describing the interaction in adsorbed layer. α is the attractive parameter, x is the size parameter and is a measure of the number of adsorbed water molecules substitute by a given inhibitor molecule. The free energy of adsorption (ΔG_{ads}) was calculated using Equations 14,15,18,23.

$$\Delta G_{ads}=-2.303\text{ RT }\log(55.5\text{ K}) \quad (14)$$

Where, R is the gas constant, T is temperature, K values obtain from the isotherms (Langmuir, Frumkin, Temkin and Florry-Huggins).

Weight loss method using response surface methodology (RSM)

Design expert software 9 was used to design the experiment. Four factors of acid concentration, inhibitor concentration, temperature and time were considered in the corrosion inhibition study. Table 1 presents the design matrix for the corrosion inhibition study. The RSM was used to examine the response and optimize the IE of *O. gratissimum* leaves extracts.

Table 1: Design matrix for the corrosion control study

Run	Factor 1, Acid concentration (M)	Factor 2, Inhibitor concentration (gm/l)	Factor 3, Temperature (K)	Factor 4, Time (h)
1	0.75	0.7	312	18
2	0.75	0.7	312	12
3	1.1	0.7	312	12
4	0.75	0.7	312	6
5	0.75	0.7	322	12
6	0.4	0.1	322	6
7	0.4	1.3	302	18
8	1.1	0.1	302	18
9	1.1	0.1	302	6
10	1.1	0.1	322	18
11	0.75	1.3	312	12
12	1.1	1.3	322	6
13	1.1	1.3	322	18
14	0.75	0.7	312	12
15	1.1	1.3	302	6
16	0.4	0.7	312	12
17	0.4	0.1	322	18
18	0.4	1.3	322	6
19	0.75	0.7	312	12
20	0.75	0.1	312	12
21	0.4	0.1	302	6
22	0.75	0.7	302	12
23	0.4	1.3	322	18
24	1.1	0.1	322	6
25	0.4	0.1	302	18
26	1.1	1.3	302	18
27	0.4	1.3	302	6
28	0.75	0.7	312	12
29	0.75	0.7	312	12
30	0.75	0.7	312	12

RESULTS AND DISCUSSION

The FTIR analysis of the leaves extract and corrosion product

The FTIR result of the *O. gratissimum* leaves extract is presented in Table 2. The *O. gratissimum* leaves extract contains S-S, C-F, C-Cl, C-Br stretch, C-H, C-O, N-H, O-H, C=O, and para-benzene functional groups. The functional groups of the corrosion products are presented in Table 3. The peaks and their corresponding intensities represent the functional groups of the plant extract. The shifts in the peaks of the functional groups indicate that there was a synergy among the functional groups in the corrosion inhibition process [18].

Table 2: The functional groups of the *Ocimum gratissimum* leaves extract

S. No.	Peak	Description of intensity	Functional group	Interpretation
1	459.1 cm^{-1}	Medium intensity saw tooth peak	S–S stretching	Disulphides
2	551.74 cm^{-1} 640.52 cm^{-1}	Strong intensity saw tooth peaks	C–F, C–Cl C–Br, C–Stretching	Halides
3	721.58 cm^{-1} 771.76 cm^{-1}	Strong intensity with blurred peak	C–H stretching	Aromatic compounds
4	818.08 cm^{-1}	Strong intensity with blurred peak	C–Cl stretching	Halogen compounds
5	918.44 cm^{-1} 980.20 cm^{-1} 1072.84 cm^{-1}	Strong intensity saw tooth peaks	C–O stretching	Ethers
6	1192.5 cm^{-1}	Strong intensity blurred peak, sharp peak	N–O stretching	Nitro compounds
7	1323.74 cm^{-1} 1404.80 cm^{-1} 1478.14 cm^{-1}	Strong intensity broad, blurred broad peaks	C–H stretching	Alkanes
8	1609.38 cm^{-1} 1748.34 cm^{-1}	Strong intensity broad peaks	C=O stretching	Acid Anhydride
9	1875.72 cm^{-1}	Very strong intensity sharp peak	C=O stretching	Acid Halides
10	2010.82 cm^{-1} 2045.56 cm^{-1}	Strong intensity broad peaks	N–H stretching	Amino acid
11	2122.76 cm^{-1}	Strong intensity sharp peak	–N ≡ stretching	Aliphatic Iso nitrite (Nitrogen containing)
12	2273.30 cm^{-1}	Strong intensity sharp peak	N–H stretching	Amino acid
13	2342.78 cm^{-1}	Strong intensity saw tooth peak	N–H stretching	Amino acid
14	2551.22 cm^{-1}	Medium intensity blurred peak	Para benzene	Benzyl compounds
15	2640 cm^{-1}	Medium intensity broad peak	C–H stretching	Aldehydes
16	2887.04 cm^{-1} 3080.04 cm^{-1} 3199.7 cm^{-1}	Low intensity blurred peaks	C–H stretching	Alkanes
17	3273.04 cm^{-1} 3396.56 cm^{-1} 3450.60 cm^{-1}	Low intensity blurred peaks	C–H stretching	Alcohols and Phenols
18	3632.62 cm^{-1} 3693.78 cm^{-1}	Strong intensity sharp peaks	O–H stretching	Alcohols
19	3848.18 cm^{-1}	Weak intensity blurred peaks	O–H stretching	Ketone
20	3917.66 cm^{-1}	Weak intensity blurred peaks	C=O stretching	

Table 3: Functional groups of the corrosion product

S. No.	Peak	Description of Intensity	Functional Group	Interpretation
1	428.22-500cm^{-1}	Weak intensity with saw tooth	S–S stretching	Disulphide
2	517.640.52 cm^{-1}	Weak intensity	C–F, C–Cl, C–Br, C–stretching	Halides
3	767.9 cm^{-1}	Weak intensity with tooth peak	C–H stretching	Aromatic compounds
4	825.8 cm^{-1}	Medium intensity with flat peak	C–Cl stretching	Halogen compounds
5	887.56–1041-96 cm^{-1}	Strong intensity with sharp tooth peak	C–O stretching	Ethers
6	1261.52 cm^{-1}	Strong intensity broad peak	N–O stretching	Nitro compounds
7	1412.52 cm^{-1}	Strong intensity with sharp peak	–C–C stretching	Aromatics
8	1470.42 cm^{-1}	Strong intensity with sharp peak	C–H stretching	Alkanes
9	1536.04 cm^{-1}	Medium intensity saw tooth	N=O stretching	Nitro compound
10	1601.66 cm^{-1} 1690.66 cm^{-1}	Medium intensity saw tooth peak	C=O stretching	Acid anhydrites
11	1752.2–1810.1 cm^{-1}	Strong intensity flat peak sharp peak	C=O stretching	Acid anhydrites
12	1875.72 cm^{-1}	Strong intensity sharp peak	C=O stretching	Acid halides
13	1999.24cm^{-1}-2064.7cm^{-1}	Strong intensity sharp peak, saw tooth.	N–H stretching	Amino acid
14	2118.9 cm^{-1}	Strong intensity blurred peak	–N ≡ stretching	(Nitrogen containing) Aliphatic Iso nitrite
15	2238.56–2369.8 cm^{-1}	Strong intensity sharp peak	N–H stretching	Amino acids
16	2427.7 cm^{-1}	Weak intensity blurred peak	O–H stretching	Acids
17	2551.22 cm^{-1}	Weak intensity blurred peak	Para benzene	Benzyl compoud
18	2640 cm^{-1}	Weak intensity saw tooth peak	C–H stretching	Aldehyde
19	2860 cm^{-1}–3126.36 cm^{-1}	Weak intensity blurred peak	C–H stretching	Alkanes
20	3203.56–3327.08 cm^{-1}	Weak intensity saw tooth peak	O–H stretching H–bonded	Alcohols and Phenols
21	3570.26–3693.78 cm^{-1}	Strong intensity sharp peak	O–H stretching	Alcohols
22	3848.18 cm^{-1}	Weak intensity blurred peak	C=O stretching	Ketone
23	3913.8–3967.84 cm^{-1}	Weak intensity blurred peak	Unknown	-

GC-MS analysis of leaves extract of *O. gratissimum*

The GC-MS chromatogram of the extracts of *O. gratissimum* is presented in Figure 1. The result shows the GC-MS chromatogram of 25 peaks of the compounds detected by the analysis of the plant extract. The peaks represent various chemical composition of the *O. gratissimum* extract.

The predominant molecular compositions of the extract include $C_{10}H_{16}$, $C_{15}H_{24}$, $C_{13}H_{20}O_2$, $C_{20}H_{40}O$, and $C_{10}H_{18}O$.

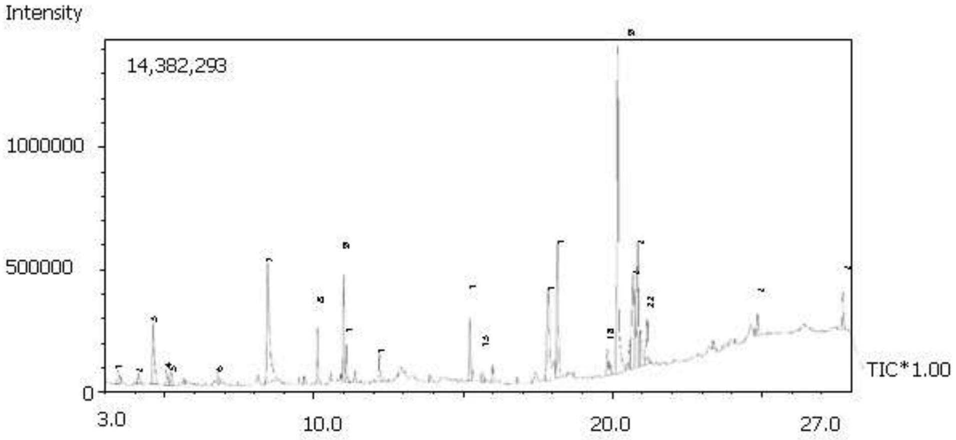


Figure 1: The GC-MS chromatogram of the *Ocimum gratissimum* leaves extract

Surface study of aluminum alloy (SEM analysis)

The micrographs of the corroded aluminum alloy in the corrosive environment (medium) in the presence and absence of the *O. gratissimum* are presented in Figure 2. Relatively, there is major damage on the aluminum surface in the absence of the extract (inhibitor).

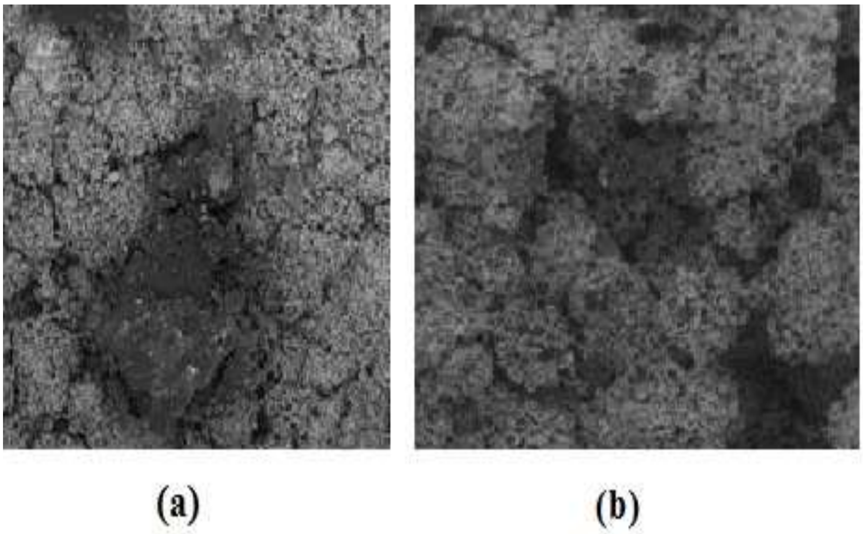


Figure 2: The micrograph of corroded aluminum in 1.1 M HCl, (a) in the absence of the extract, (b) in the presence of the extract

Results of the corrosion inhibition as determined by thermometric method

The effect of the concentration of the inhibitor on the reaction number and inhibition efficiencies of the inhibitor is presented in Table 4. Increased concentration of the inhibitor reduces the reaction number, but increases the IE. Highest IE of 81.94% was obtained at inhibitor concentration of 1.3 gm/l. The recorded high efficiency suggests that the extract can be applied for surface treatment of aluminum in HCl medium.

Table 4: Effect of concentration of *Ocimum gratissimum* leaves extract on the IE (%) for aluminium alloy in 1.1 M HCl

Inhibitor concentration (g/l)	RN	IE (%)
0.0	0.12806	-
0.1	0.06748	47.3088
0.2	0.05277	58.7933
0.3	0.03802	70.3112
0.7	0.02810	78.054
1.3	0.02312	81.9449

Result of weight loss method of corrosion inhibition study

Result of weight loss method using one factor at a time: The experimental results of weight loss method are presented in Tables 5-7. The results showed the effects of concentration, temperature and time on weight loss, corrosion rate, IE and degree of surface coverage at various concentrations of the HCl medium. Increased in acid concentration, temperature and time increases the weight loss and corrosion rate of the aluminum alloy, while increased in inhibitor concentration increases the IE and degree of surface coverage. This is in agreement with previous study [6,17,19].

Table 5: Weight loss, corrosion rate, IE and surface coverage of aluminium alloy in 1.1 M HCl with *Ocimum gratissimum* leaves extract

Inhibitor Conc. (gm/l)	Time (h)	Weight loss			Corrosion rate			IE (%)			Surface coverage (ϴ)		
		302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K
0.0	18	0.85	0.88	0.90	0.85	0.88	0.90						
0.10		0.49	0.52	0.53	0.49	0.52	0.53	42.35	40.91	41.11	0.42	0.41	0.41
0.70		0.36	0.37	0.39	0.36	0.37	0.39	57.65	57.95	56.67	0.58	0.58	0.57
1.30		0.22	0.26	0.27	0.22	0.26	0.27	74.12	70.45	70.00	0.74	0.71	0.70
Inhibitor Conc. (gm/l)	**Time (h)**	**Weight loss**			**Corrosion rate**			**IE (%)**			**Surface coverage (ϴ)**		
		302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K
0.0	12	0.85	0.88	0.90	5.90	6.11	6.25						
0.10		0.49	0.52	0.53	3.40	3.61	3.68	42.35	40.91	41.11	0.42	0.41	0.41
0.70		0.36	0.37	0.39	2.40	2.57	2.71	57.65	57.95	56.67	0.58	0.58	0.57
1.30		0.22	0.26	0.27	1.53	1.81	1.88	74.12	70.45	70.00	0.74	0.71	0.70
Inhibitor Conc. (gm/l)	**Time (h)**	**Weight loss**			**Corrosion rate**			**IE (%)**			**Surface coverage (ϴ)**		
		302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K
0.0	6	0.78	0.80	0.81	10.83	11.11	11.25						
0.10		0.46	0.50	0.52	6.39	6.94	7.22	41.03	37.50	36.00	0.41.	0.38	0.36
0.70		0.33	0.36	0.38	4.58	5.00	5.28	57.69	55.00	53.09	0.58	0.55	0 53
1.30		0.20	0.25	0.26	2.78	3.47	3.61	74.36	68.75	67.90	0.74	0.69	0.68

Table 6: Weight loss, corrosion rate, inhibition efficiency and surface coverage of AA in 0.75 M HCl with *Ocimum gratissimum* leaves extract

Inhibitor Conc.(g/l)	Time (h)	Weight loss			Corrosion rate			IE (%)			Surface coverage (ϴ)		
		302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K
0.0	18	0.86	0.87	0.90	3.98	4.03	4.17						
0.10		0.38	0.42	0.46	1.76	1.94	2.13	55.81	51.72	48.49	0.56	0.52	0.49
0.70		0.30	0.33	0.36	1.39	1.53	1.67	65.12	62.07	60.00	0.65	0.62	0.60
1.30		0.15	0.18	0.21	0.69	0.83	0.97	82.56	79.31	76.67	0.83	0.79	0.77
Inhibitor Conc. (gm/l)	**Time (h)**	**Weight loss**			**Corrosion rate**			**IE (%)**			**Surface coverage (ϴ)**		
		302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K
0.0	12	0.82	0.83	0.84	5.69	5.76	5.83						
0.10		0.36	0.41	0.42	2.50	2.85	2.92	56.10	50.60	50.00	0.56	0.51	0.50
0.70		0.29	0.31	0.33	2.01	2.15	2.29	64.63	62.65	60.71	0.65	0.63	0.61
1.30		0.14	0.15	0.19	0.97	1.04	1.32	82.93	81.93	77.38	0.83	0.82	0.77
		Weight loss			**Corrosion rate**			**IE (%)**			**Surface coverage (ϴ)**		
		302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K
0.0	6	0.70	0.73	0.75	9.72	10.14	10.42						
0.10		0.34	0.36	0.38	4.72	5.00	5.28	51.43	50.68	49.00	0.54	0.51	0.49
0.70		0.28	0.30	0.32	3.89	4.17	4.44	60.00	58.90	57.33	0.60	0.59	0.57
1.30		0.12	0.14	0.16	1.67	1.94	2.22	82.86	80.82	78.67	0.83	0.81	0.79

Table 7: Weight loss, corrosion rate, inhibition efficiency and surface coverage of AA in 0.40 M HCl with *Ocimum gratissimum* leaves extract

Inhibitor Conc.(gm/l)	Time (h)	Weight loss			Corrosion rate			IE (%)			Surface coverage (ϴ)		
		302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K
0.0	18	0.81	0.83	0.85	3.75	3.84	3.94						
0.10		0.36	0.41	0.43	1.67	1.90	1.99	55.56	50.60	49.41	0.56	0.51	0.49
0.70		0.28	0.32	0.35	1.30	1.48	1.62	65.43	61.45	58.82	0.65	0.62	0.59
1.30		0.15	0.19	0.21	0.69	0.88	0.97	81.48	77.11	76.67	0.82	0.77	0.75
Inhibitor Conc. (gm/l)	**Time (h)**	**Weight loss**			**Corrosion rate**			**IE (%)**			**Surface coverage (ϴ)**		
		302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K
0.0	12	0.75	0.76	0.78	5.21	5.28	5.42						
0.10		0.34	0.36	0.39	2.36	2.50	2.71	54.67	52.63	50.00	0.55	0.53	0.50
0.70		0.27	0.29	0.31	1.88	2.01	2.15	64.00	61.84	60.26	0.64	0.62	0.60
1.30		0.14	0.17	0.19	0.97	1.18	1.32	81.33	77.63	75.64	0.81	0.78	0.76
		Weight loss			**Corrosion rate**			**IE (%)**			**Surface coverage (ϴ)**		
		302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K	302 K	312 K	322 K
0.0	6	0.58	0.60	0.62	8.06	8.33	8.61		-2E-14			-2E-16	
0.10		0.32	0.34	0.36	4.44	4.72	5.00	44.83	43.33	42.00	0.45	0.43	0.42
0.70		0.25	0.27	0.30	3.47	3.75	4.17	56.90	55.00	60.00	0.57	0./55	0.60
1.30		0.12	0.14	0.17	1.67	1.94	2.36	79.31	76.67	77.33	0.79	0.77	0.77

The activation energy and heat of adsorption for the corrosion inhibition of aluminium alloy

The results of the activation energy and heat of adsorption (Q_{ads}) for the corrosion inhibition of aluminium alloy in the acid medium with *O. gratissimum* extract are presented in Table 8. The values of the activation energy are positive in all cases signifying that the reaction is spontaneous. The negative values of the heat of adsorption showed that the adsorption of the extract on the aluminum surface is exothermic [6,15,23]. The heat of adsorption has positive values for the inhibitor concentration of 0.3 gm/l and 0.5 gm/l. It may be as a result of the formation of oxide film on the aluminum surface before the reaction proceeds.

Table 8: The activation energy and heat of adsorption (Q_{ads}) of the process

Concentration of plant extract (g/l)	Activation energy (kJ/mol)	Heat of adsorption (Q_{ads}) (kJ/mol)
0.1	9.831	-2.508
0.3	6.283	0.584
0.5	6.580	0.326
0.7	13.548	-4.484
1.3	26.810	-11.065

Fitting of data into the adsorption isotherms

The experimental data were fitted into Langmuir Isotherm (Figure 3). The plots of log (C/Θ) versus logC shows linear graph [18,15]. Considering the fitted data to the Langmuir isotherm, the R^2 values are close to unity, indicating strong adherence to the Langmuir adsorption isotherm [17].

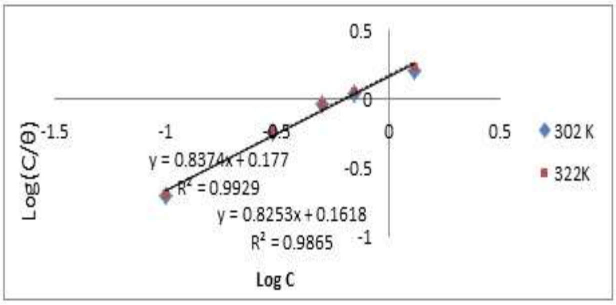


Figure 3: The plot of log (C/θ) versus log C for aluminium alloy at 302 K and 322 K with *Ocimum gratissimum*

The data were fitted into the Frumkin adsorption isotherm. Plots of Log (C) × (Θ / (1 − Θ)) againstΘ) was linear graph (Figure 4). It showed an adherence to the Frumkin isotherm.

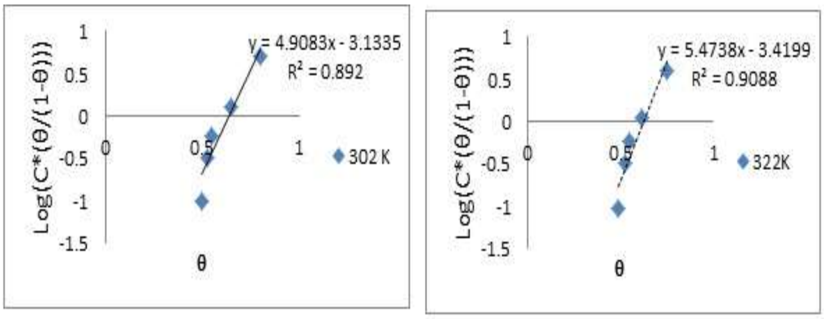


Figure 4: Plot of log $(C) \times (\theta/((1-\theta)))$ versus θ for aluminium alloy at 302 K and 322 K with *Ocimum gratissimum*

The experimental data was fitted into Temkin adsorption isotherm as shown in Figure 5. The plot of Θ against logC from was linear [18]. This showed an adherence to the Temkin adsorption isotherm.

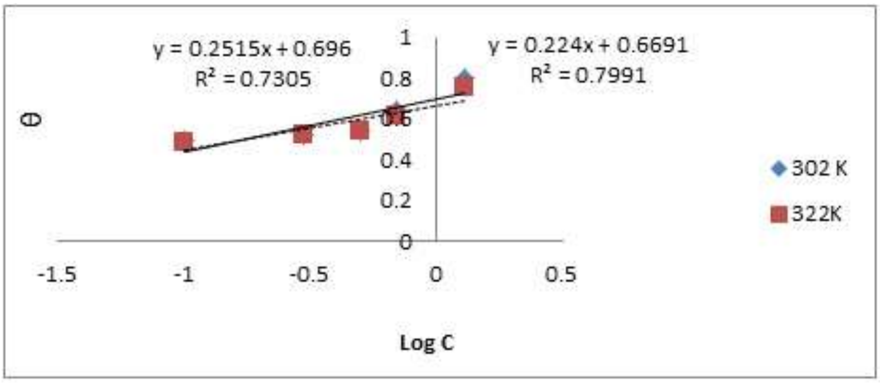


Figure 5: The Plot of θ versus logC for aluminium alloy at 302K and 322K with *Ocimum gratissimum*

The experimental data were fitted into the Flory-Huggins adsorption isotherm as shown in Figure 6. From the Flory-Huggins isotherm, plots of log (θ/C) versus log $(1-\theta)$ gave a linear relationship. The linearity signified that Flory-Huggins isotherm was adhered to [18].

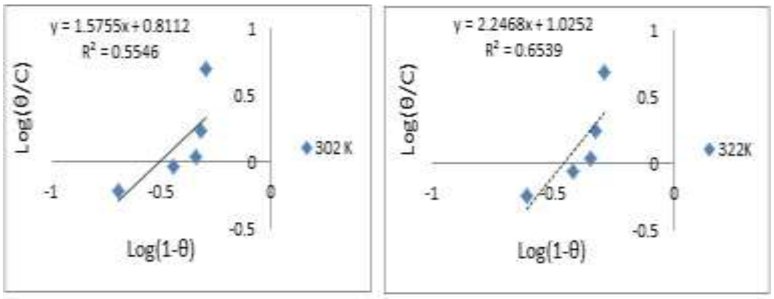


Figure 6: Plot of log (θ/C) Versus log (1-θ) for aluminium alloy at 302 K and 322 K with *Ocimum gratissimum*

The adsorption parameters for the corrosion inhibition

The adsorption parameters for the corrosion inhibition of aluminum alloy in HCl medium, are presented in Table 9. The values of the R^2 were all positive, indicating that the adsorption of the extract on aluminum surface obeyed physical adsorption mechanism. The values of the size parameter were positive, which signifies bulky adsorption layer. The free energy of adsorption value (ΔG_{ads}) was less than the threshold value of −40 kJ/mol. Hence the adsorption of the extract on the surface of the aluminum alloy was spontaneous and favored the mechanism of physical adsorption.

Table 9: The adsorption parameters of the extract in HCl aluminium alloy at 302 K and 322 K

Adsorption isotherm	Temperature (K)	R^2	LogK	K	$\Delta G_{(ads)}$ (kJ/mol)	Isotherm property
Langmuir Isotherm	302 322	0.986 0.992	-0.161 -0.177	0.690 0.665	-9.15 -9.66	- -
Frumkin Isotherm	302 322	0.892 0.908	-1.360 -1.485	0.044 0.033	-2.24 -1.62	a=2.454 a=2.737
Temkim Isotherm	302 322	0.730 0.799	2.773 2.987	592.93 970.51	-26.12 -29.17	α=-4.588 α=-5.141
Flory-Huggins Isotherm	302 322	0.554 0.653	0.811 1.025	6.471 10.59	-14.78 -17.07	x=1.575 x=2.246

Result of weight loss using RSM

The result of the 30 runs of the experiment for the weight loss method using RSM is presented in Table 10. The results show the values of the four considered factors (temperature, acid concentration, inhibitor concentration and time) and the corresponding responses of weight loss, corrosion rate and inhibition efficiency. The Figure 7(a-g) represent the plot of (a) Predicted versus actual IE (%), (b) IE (%) versus inhibitor concentration (gm/l) and acid concentration (M), (c) IE (%) versus temperature(K) and acid concentration (M), (d) IE (%) versus time (h) and acid concentration (M), (e) IE (%) versus temperature (K) and inhibitor concentration (gm/l), (f) IE (%) versus time (h) and inhibitor concentration (gm/l), (g) IE (%) versus time (h) and temperature (K), for different concentrations of *O. gratissimum* with aluminium alloy in HCl. The predicted versus actual IE showed a linear graph indicating that the Design Expert software was adequate for the description of the inhibition process. The IE increases with increase in inhibitor concentration but reduces with increase in temperature.

Table 10: The RSM result for *Ocimum gratissimum* leaves extract in HCl with aluminium alloy

Run	Factor 1, Acid Conc. (M)	Factor 2, Inhibitor Conc. (gm/l)	Factor 3, Temperature (K)	Factor 4, Time (h)	Response 1, Weight loss (gm)	Response 2, Corrosion rate ($mg/cm^2.h$)	Response 3, IE (%)
1	0.75	0.7	312	18	0.33	1.528	62.07
2	0.75	0.7	312	12	0.3	2.083	63.86
3	1.1	0.7	312	12	0.32	2.222	63.64
4	0.75	0.7	312	6	0.36	5	50.68
5	0.75	0.7	322	12	0.33	2.292	60.71
6	0.4	0.1	322	6	0.37	5.139	40.32
7	0.4	1.3	302	18	0.15	0.694	81.48
8	1.1	0.1	302	18	0.45	2.083	50.00
9	1.1	0.1	302	6	0.4	5.556	48.72
10	1.1	0.1	322	18	0.5	2.315	48.45
11	0.75	1.3	312	12	0.15	1.042	81.93
12	1.1	1.3	322	6	0.2	2.778	75.31
13	1.1	1.3	322	18	0.24	1.111	75.26
14	0.75	0.7	312	12	0.3	2.083	63.86
15	1.1	1.3	302	6	0.16	2.222	79.49
16	0.4	0.7	312	12	0.3	2.083	60.53
17	0.4	0.1	322	18	0.43	1.991	49.41
18	0.4	1.3	322	6	0.18	2.5	70.97
19	0.75	0.7	312	12	0.3	2.083	63.86

20	0.75	0.1	312	12	0.4	2.778	51.81
21	0.4	0.1	302	6	0.33	4.583	43.10
22	0.75	0.7	302	12	0.28	1.944	65.85
23	0.4	1.3	322	18	0.21	0.972	75.29
24	1.1	0.1	322	6	0.47	6.528	41.98
25	0.4	0.1	302	18	0.37	1.713	54.32
26	1.1	1.3	302	18	0.18	0.833	80.00
27	0.4	1.3	302	6	0.13	1.806	77.59
28	0.75	0.7	312	12	0.3	2.083	63.86
29	0.75	0.7	312	12	0.3	2.083	63.86
30	0.75	0.7	312	12	0.3	2.083	63.86

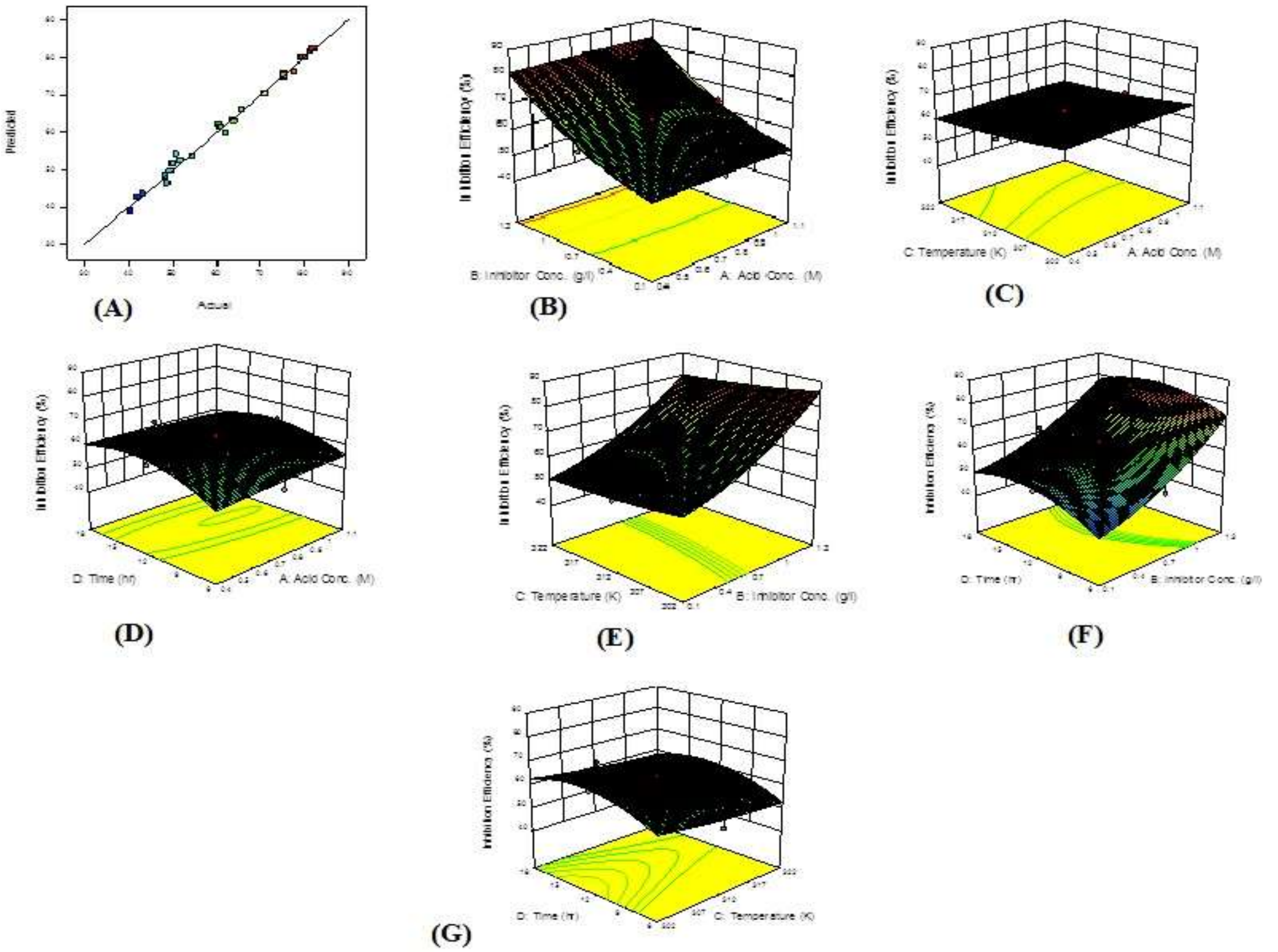


Figure 7: The IE (%) of *Ocimum gratissimum* leaves extract as corrosion inhibitor of aluminium alloy in HCl

Optimum IE of 80.09% at optima acid concentration of 1.1 M, inhibition concentration of 1.3 gm/l, temperature of 312 K and time of 6 h was obtained. It showed that the extract can be used for corrosion control of aluminum in HCl medium. The mathematical model for the IE of *O. gratissimum* leaves extract as corrosion inhibitor of aluminium alloy in HCl medium is presented in Equation 15. The model showed the relationship among the IE, acid concentration (A), inhibitor concentration (B), temperature (C) and time (D). The models in terms of coded factors predicts the response for a given levels of each factor. It also shows the relative impact of each factor.

$$IE = + 63.17 + 0.55*A + 14.96*B - 2.38*C + 2.67*D + 0.17*A + 0.21*AC - 1.27*AD - 0.36*BC - 1.21*BD + 0.18*CD - 0.39*A^2 + 4.40*B^2 + 0.81*C^2 - 6.10*D^2 \qquad (15)$$

In terms of the significant terms, the model of Equations (15) is reduced to Equation 16:

$$IE = + 63.17 + 14.96 * B - 2.38 * C + 2.67 * D - 1.27 * AD - 1.21 * BD + 4.40 * B^2 - 6.10D^2 \qquad (16)$$

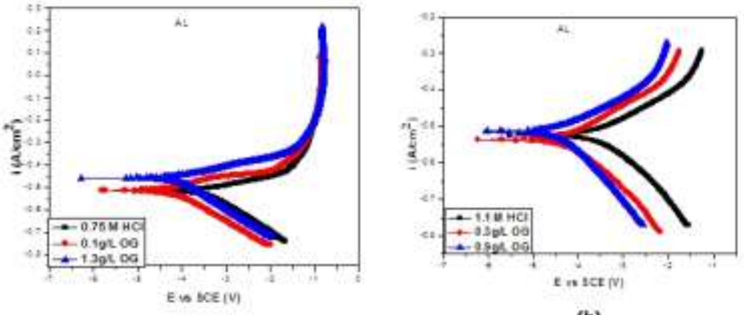
The Analysis of Variance (ANOVA) is presented in Table 11. From Table 11, the Model F-value of 118.95 implies the model is significant. Values of "Prob>F" less than 0.0500 indicate model terms are significant. In this case B, C, D, AD, BD, B^2, D^2 are significant model terms. The "Pred R-Squared" of 0.9542 is in reasonable agreement with the "Adj R-Squared" of 0.9827; the difference is less than 0.2. The generated quadratic model can adequately describe the corrosion inhibition process.

Table 11: ANOVA for the corrosion inhibition process

Source	Sum of squares	Df	Mean square	F-value	P-value Prob>F
Model	4438.42	14	317.03	118.95	<0.0001 significant
(A) Acid Conc.	5.38	1	5.38	2.02	0.1759
(B) Inhibitor conc.	4026.33	1	4026.33	1510.70	<0.0001
© Temperature	102.01	1	102.01	38.27	<0.0001
D–Time	128.64	1	128.64	48.27	<0.0001
AB	0.47	1	0.47	0.17	0.6818
AC	0.68	1	0.68	0.25	0.6217
AD	25.78	1	25.78	9.67	0.0072
BC	2.07	1	2.07	0.78	0.3925
BD	23.50	1	23.50	8.82	0.0096
CD	0.54	1	0.54	0.20	0.6601
A^2	0.38	1	0.38	0.14	0.7093
B^2	50.15	1	50.15	18.82	0.0006
C^2	1.70	1	1.70	0.64	0.4372
D^2	96.26	1	96.26	36.12	<0.0001
Residual	39.98	15	2.67		
Lack of fit	39.98	10	4.00		
Pure error	0.000	5	0.000		
Corr Total	4478.40	29			

Potentiodynamic polarization measurement

The potentiodynamic polarization curve is shown in Figure 8. The *O. gratissimum* leaves extract inhibits both cathodic and anodic reactions and behave like a mixed-type inhibitors.



(a) (b)

Figure 8: Potentiodynamic polarization curves of aluminium alloy with *Ocimum gratissimum* leaves extract in: (a) 0.75 M HCl Solution; (b) 1.10 M HCl solution

The parameters of Tafel polarization of the aluminum alloy immersed in 0.75 M HCl and 1.10 M HCl in the presence and absence of *O. gratissimum* inhibitor are presented in Table 12.

Table 12: Polarization parameters for aluminum in HCl solution in the absence and presence of *Ocimum gratissimum* leaves extract

System	E_{corr}	I_{corr}	ϴ	IE (%)
1.1 M HCl	-536.4	107.2		
0.1 g/l *O. gratissimum*	-548.2	60.5	0.451	43.6
1.3 g/l *O. gratissimum*	-541.9	13.2	0.873	87.7
0.75 M HCl	-550.4	87.3		
0.1 g/l *O. gratissimum*	-549.2	49.6	0.431	43.2
1.3 g/l *O. gratissimum*	-552.9	9.5	0.907	89.1

Electrochemical impedance spectroscopy (EIS)

Figure 9 presents the impedance response of aluminum alloy in the presence of *O. gratissimum* leaves extract in 0.75 M HCl and 1.10 M HCl. The Nyquist plots in each case reveal a depressed capacitive semicircle over the frequency range investigated; this shows one time constant in the Bode plots. The electrochemical impedance parameters of the corrosion inhibition of aluminum in HCl medium are shown in Table 13. The C_{dl} represents double layer capacitance. It changes in value because of the modification of the medium in the presence of the inhibitor.

Table 13: Electrochemical impedance parameters of aluminium alloy in HCl Solution in the absence and presence of *Ocimum gratissimum* leaves extract

System	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	N	C_{dl} (F cm^{-2})	IE
1.1 M HCl	1.659	300.7	0.89	0.00006908	
0.1 gm/l *O. gratissimum*	2.608	660.5	0.83	0.00006982	54.5

1.3 gm/l *O. gratissimum*	2.238	3450	0.83	0.00006033	91.3
0.75 M HCl	2.06	480.6	0.89	0.0001131	
0.1 gm/l *O. gratissimum*	3.32	780	0.89	0.00003282	38.4
1.3 gm/l *O. gratissimum*	3.46	3000	0.89	0.00002972	84.1

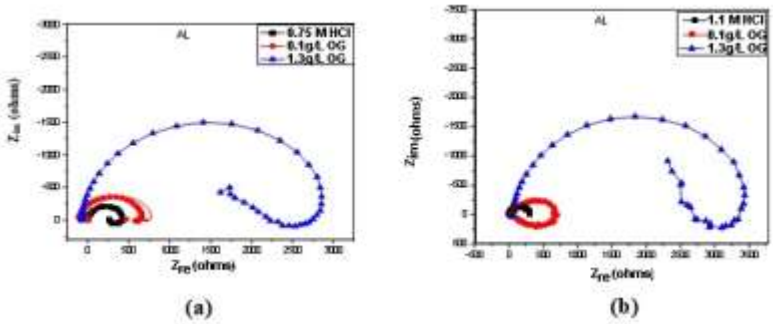


Figure 9: Impedance spectra of alluminium alloy with *Ocimum gratissimum* leaves extract in: (a) 0.75 M HCl solution (b) 1.10 M HCl solution

CONCLUSION

Considering the analysis of the experimental results, the following conclusions can be made: There was a synergy among the functional groups and molecular compounds of the extract in the corrosion inhibition process. The free energy of adsorption value (ΔG_{ads}) was less than the threshold value of-40 kJ/mol. The adsorption of the extract on the surface of the aluminum alloy was spontaneous and favored the mechanism of physical adsorption. Quadratic model was adequate for the description of the IE as a function of the considered factors of the inhibition process. Optimum IEof 80.09% at acid concentration of 1.1 M, inhibitor concentration of 1.3 gm/l, temperature of 312 K and time of 6 hrs was obtained. The plant extract was identified as mixed-type inhibitor that can control both the anodic and cathodic corrosion. All results of the applied techniques are in agreement of recording high inhibition efficiency. The extract can effectively control corrosion in HCl medium.

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