



Inhibition study of *Andrographis paniculata* plants extract for the corrosion control Of Aluminum in hydrochloric acid medium

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Abstract : The inhibitive effect of *Andrographis panniculata* plants extract (APPE) on the corrosion control of aluminum was investigated in hydrochloric acid medium of pH=3 using Tafel polarization and electrochemical impedance spectroscopy (EIS) techniques in the temperature range of 303 to 323K. The concentration of inhibitor used was in the range of 0.05–0.4g L⁻¹. The surface morphology was studied using scanning electron microscopy (SEM) and EDX. The kinetic and thermodynamic parameters were calculated and discussed in detail. Inhibition efficiency was found to increase with increasing inhibitor concentration and decrease with temperature. APPE acted as an anodic type of inhibitor at lower concentrations of inhibitor and mixed type at higher concentrations of inhibitor. Optimum inhibition efficiency of 91.55% was achieved at 0.4g L⁻¹ of APPE. Adsorption of inhibitor was through both physisorption and chemisorption on the surface of the metal. Adsorption of the inhibitor obeyed Langmuir adsorption isotherm. The results obtained by both the methods were in good agreement with one another. A suitable mechanism was proposed for the corrosion inhibition process. Surface studies confirmed the adsorption of inhibitor onto the surface of the metal. APPE emerged as a potential, cost effective and eco-friendly natural inhibitor for the corrosion control of aluminum in hydrochloric acid medium.

Keywords: Aluminum, Green inhibitor, *Andrographis paniculata* plants, Tafel polarisation, EIS studies, SEM.

Introduction

Aluminum and its alloys are very important materials used in industrial and domestic purposes due to their low cost, light weight, excellent thermal and electrical conductivities, good forming properties and other relatively noble properties. The excellent corrosion resistance of aluminum and its alloys are largely due to its affinity for oxygen, this results in the formation of a very thin, but tenacious oxide film which covers the surface as soon as a freshly-cut piece of the metal is exposed to the atmosphere¹.

Hydrochloric acid in the pH range of 2–4.5 is mainly used for pickling, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing, acid descaling, chemical and electrochemical etching of aluminum and its alloys². These exposure usually lead to loss of the metal due to corrosion. The protection of aluminum, aluminum alloys and its oxide films against the corrosive action of chloride ions have been extensively studied⁴⁻⁵. A useful method to protect metals and alloys deployed in service in aggressive environments against corrosion is the addition of inhibitors⁶. Despite of broad spectrum of organic compounds,

the choice of appropriate inhibitor for a particular application is restricted by several factors such as increased environmental awareness, high cost, non-bio-degradability and toxicity.

The exploration of natural products of plant origin as non-expensive eco-friendly inhibitor is an essential field study⁷. Till date lots of works have been reported for using natural product as corrosion inhibitors^{8,9} for aluminum in acidic medium.

We report herein, the results of utility of *Andrographis paniculata* plants extract (APPE) for the corrosion control of aluminum in hydrochloric acid medium of pH=3. *Andrographis paniculata* plants extract (APPE) is reported to contain numerous organic heterocyclic compounds. Major constituents are reported to be lactone andrographolide, 5,7,2¹,3¹-tetramethoxy flavanone and 5-hydroxy 7, 2¹,3¹- trimethoxy flavanone¹⁰.

Experimental

1. Material

The experiments were performed with specimens of aluminum. Composition of material used is given in the Table 1. Cylindrical test coupons of 10 mm diameter and approximately 20mm height were machined from the rods of aluminum and metallographically mounted up to 10mm height using cold setting resin. The exposed flat surface of the mounted part was polished as per standard metallographic practice - belt grinding followed by polishing on emery papers (in the range of 600-2000) and finally on disc polishing wheel using levigated alumina abrasive.

Table 1: Composition of material

Element	Si	Fe	Mg	Al
Composition (weight %)	0.467	0.163	0.530	Balance

2. Preparation of medium

The stock solution of 2M hydrochloric acid was prepared by using analar grade hydrochloric acid and double distilled water. Standardization was done by volumetric method.

3. Preparation and characterization of the inhibitor

3.1. Inhibitor solution preparation

Andrographispaniculata plants extract (APPE) was prepared by literature method¹⁰.

3.2. Spectral studies of aqueous plant extract

FTIR spectrum of the dried sample was recorded using spectrophotometer (Shimadzu model) in the frequency range of 4000 to 400cm⁻¹ using KBr pellet technique.

4. Electrochemical measurements

Electrochemical studies were carried out using an electrochemical workstation (CH600D-series, U.S.model, CH Instruments with beta software). Studies were done by using conventional three electrode Pyrex glass cell with platinum as counter electrode and SCE as reference electrode. Working electrode was aluminum. Finely polished aluminum specimen was exposed to hydrochloric acid of pH =3 at different temperatures (30 °C to 50 °C) and allowed to establish a steady state open circuit potential by immersing the electrodes in corrosive medium for 1800 seconds. Experiments were performed by placing the cell in a calibrated thermostat and under unstirred conditions.

Potentiodynamic polarization studies and electrochemical impedance spectroscopy studies were carried out as per the reported literature.

5.Scanning electron microscopy (SEM) and Energy –dispersive X-ray spectroscopy (EDX) analysis:

The surface morphology of aluminum surface, in the presence and absence of the inhibitor was studied by immersing the material in hydrochloric acid medium of pH=3 for 2 h. using JEOL JSM-6380L Analytical scanning electron microscope. EDX investigation was carried out to study the elemental mapping.

Results and discussions

1. Potentiodynamic polarization (PDP) method

Figure 1 shows the potentiodynamic polarization plot for the corrosion of aluminum in hydrochloric acid medium of pH=3 containing different concentrations of APPE at 30 °C.

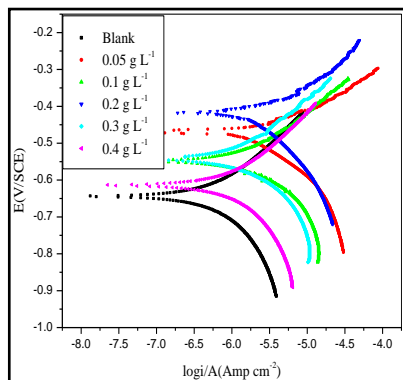


Figure 1: Potentiodynamic polarization plot for the corrosion of aluminum containing different concentrations of APPE in HCl of pH=3 at 30°C.

Valuable potentiodynamic polarization parameters like, corrosion current density ($i_{\text{corr.}}$), corrosion potential ($E_{\text{corr.}}$), anodic Tafel slope (β_a) and cathodic Tafel slope ($-\beta_c$) were obtained from the potentiodynamic polarization plots. Corrosion rate was calculated using equation (1) ¹¹.

$$\text{C. R. (mmY}^{-1}\text{)} = \frac{i_{\text{corr.}} \times M \times 3270}{\rho \times Z} \quad (1)$$

where 3270 is a constant that defines the unit of corrosion rate, i_{corr} = corrosion current density in A cm^{-2} , ρ = density of the corroding material (in g cm^{-3}), M = Atomic mass of the metal, and Z = Number of electrons transferred per metal atom. For aluminum $Z= 27$ and $\rho = 2.7 \text{ g cm}^{-3}$

Percentage inhibition efficiency was calculated using the equation (2)

$$\text{I.E. (\%)} = \theta \times 100 \quad (2)$$

$$\text{where } \theta = \frac{i_{\text{corr.}} - i_{\text{corr. (inh)}}}{i_{\text{corr.}}} \quad (3)$$

where $i_{\text{corr.}}$ and $i_{\text{corr. (inh)}}$ are the corrosion current densities in absence and in the presence of inhibitor, respectively. From the corrosion potential ($E_{\text{corr.}}$), corrosion current density ($i_{\text{corr.}}$), corrosion rate (CR) and percentage inhibition efficiency (% I.E) were calculated. The results of the potentiodynamic polarization measurements are tabulated in Table2.

Table 2: Results of potentiodynamic polarization and electrochemical impedance spectroscopy measurements for the corrosion of aluminum in hydrochloric acid medium of pH=3 containing different concentrations of APPE at different temperatures.

Temp. (°C)	PDP				EIS			
	[APPE] (g L ⁻¹)	i _{corr.} (μA. cm ⁻²)	-β _c (mV dec ⁻¹)	E _{corr.} (mV vs SCE)	%I.E.	C _{dl} (×10 ⁻¹⁰ F cm ⁻²)	R _p (ohm cm ²)	%I.E.
30	0.0	7.05	603	-654	-----	32.9	6068	----
	0.05	1.25	691	-469	82.23	12.2	23933	74.6
	0.1	0.82	586	-548	88.36	6.9	25653	76.3
	0.2	0.75	491	-417	89.24	3.9	40057	84.8
	0.3	0.70	563	-642	89.96	2.5	48956	87.6
	0.4	0.59	489	-614	91.55	0.5	73891	91.7
35	0.0	7.49	644	-659	-----	111.0	6036	----
	0.05	1.40	642	-474	81.36	13.9	20909	71.1
	0.1	1.07	605	-474	85.65	8.0	22300	72.9
	0.2	0.91	557	-518	87.87	4.8	28017	78.4
	0.3	0.85	541	-650	88.69	2.6	40057	84.9
	0.4	0.74	461	-599	90.06	1.2	48956	87.6
40	0.0	7.97	651	-546	-----	158.0	6013	----
	0.05	2.65	756	-472	66.80	15.4	11770	69.5
	0.1	1.50	659	-443	81.18	9.0	18300	67.7
	0.2	1.11	529	-553	86.06	5.0	26829	77.5
	0.3	1.01	540	-583	87.31	5.8	37385	83.9
	0.4	0.91	586	-545	88.64	1.9	46361	86.7
45	0.0	9.22	615	-633	-----	461.0	4550	----
	0.05	3.04	632	-482	66.92	33.2	10534	56.8
	0.1	2.17	538	-487	76.44	11.8	16122	71.7
	0.2	1.61	530	-538	82.46	6.9	20640	76.9
	0.3	1.32	540	-560	85.58	4.3	27286	83.3
	0.4	1.16	747	-593	87.38	2.8	31561	85.5
50	0.0	9.33	505	-665	-----	552.0	4363	----
	0.05	4.33	495	-477	53.65	48.1	9574	54.4
	0.1	2.85	637	-524	69.45	21.7	14779	70.4
	0.2	2.14	559	-530	77.10	8.8	19771	77.9
	0.3	1.66	586	-642	82.17	6.6	26017	83.2
	0.4	1.27	489	-613	86.38	4.1	28128	84.4

With increase in concentrations of APPE corrosion current density decreased. Inhibition efficiency increased with increasing inhibitor concentrations. The observed inhibition efficiency of APPE may be due to the adsorption of its components on the aluminum surface. The adsorbed molecules may isolate the metal surface from the aggressive medium leading to decrease in the corrosion rate⁷.

The anodic branches of potentiodynamic polarization plots showed the inflection points at potentials more positive than corrosion potential (E_{corr.}), characterized by two different slopes indicating a kinetic barrier effect, possibly due to the deposition of a surface film followed by its dissolution at increased anodic potential¹¹. However, the cathodic branch of polarization curves showed linear and cathodic Tafel slopes remained almost unchanged for uninhibited and inhibited solutions. This indicated that inhibitive action of APPE may be due to simple blocking of the available surface area on the metal surface^{12,13}.

There was measurable positive shift (in the range of 86mV to 250mV) in corrosion potential (E_{corr.}) after the addition of inhibitor (0.05–0.2g L⁻¹) at lower concentrations. According to Li et al¹⁴, if the displacement in corrosion potential after the addition of inhibitor is more than ±85 mV with respect to corrosion potential of the uninhibited solution, then the inhibitor can be considered distinctively as a cathodic or anodic type. In the

present investigations for hydrochloric acid medium of pH=3 for lower concentrations (0.05–0.2 g L⁻¹) of inhibitor, shift in the corrosion potential was more than 85mV, towards the positive direction. This observation suggested that constituents of the inhibitor molecule may act as anodic type of inhibitor and brings the anodic reaction under control. But at higher concentrations of inhibitor the shift in corrosion potential was less than ±85 mV (in the range of 1mV– 80mV) with potential slightly shifted towards positive direction. This observation suggested that constituents of inhibitor molecule acts as mixed type and brings both anodic and cathodic reactions under control with preferentially bringing down the anodic reaction under control.

2. Electrochemical impedance spectroscopy (EIS) technique

Figure 2 represent the Nyquist plot for the corrosion of aluminum in hydrochloric acid medium of pH=3 containing different concentrations of APPE at 30 °C. Similar plots were obtained under other studied temperatures.

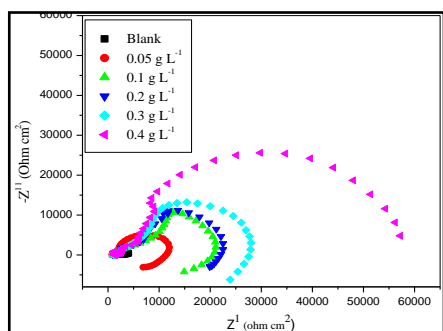


Figure 2: Nyquist plot for the corrosion of aluminum in HCl of pH=3 containing different concentrations of APPE at 30°C.

The impedance plots are semicircles. It indicates that the corrosion process is mainly charge transfer controlled. The presence of inhibitor increased the impedance but did not change the mechanism of corrosion. These are in accordance with the observations obtained from the polarization measurements that the inhibitor does not alter the mechanism of electrochemical reactions responsible for corrosion. It inhibits corrosion primarily through adsorption of the inhibitor on the metal surface¹⁵. The impedance plots are with a depressed capacitive loop at high-frequency range (HF) followed by an inductive loop at low-frequency (LF) region. Similar impedance plots have been reported in the literature for the corrosion of pure aluminum and aluminum alloys in various electrolytes¹⁶.

The high frequency capacitive loop could be assigned to the charge transfer of the corrosion process and to the formation of oxide layer. The oxide film is considered to be a parallel circuit of a resistor due to the ionic conduction in the oxide film and a capacitor due to its dielectric properties. According to Brett¹⁶, the capacitive loop is corresponding to the interfacial reactions, particularly, the reaction of aluminum oxidation at the metal/oxide/electrolyte interface. The process includes the formation of Al⁺ ions at the metal/oxide interface, and their migration through the oxide/solution interface where they are oxidized to Al³⁺. At the oxide/solution interface, OH⁻ or O²⁻ ions are also formed. The fact that all the three processes are represented by only one loop could be attributed either to the overlapping of the loops of processes, or to the assumption that one process dominates and, therefore, excludes the other processes. The other explanation offered to the high frequency capacitive loop is the oxide film itself. This was supported by a linear relationship between the inverse of the capacitance and the potential found by Bessone et al.¹⁷ and Wit and Lenderink¹⁴. The origin of the inductive loop has often been attributed to surface or bulk relaxation of species in the oxide layer¹⁵. The LF inductive loop may be related to the relaxation process obtained by adsorption and incorporation of sulfate ions, oxide ion and charged intermediates on and into the oxide film. As the inhibitor concentrations increased the diameter of the inductive loop went on decreasing which may be due to the increase in the adsorption of inhibitor indicating decrease in the relaxation process.

As shown in Figure 2 the obtained semicircles in absence or in presence of inhibitor were depressed. Deviation of this kind is referred to as frequency dispersion. It has been attributed to in-homogeneities of solid surfaces. Mansfeld et al.¹¹ have suggested an exponent 'n' in the impedance function as a deviation parameter

from the ideal behavior. By this suggestion, the capacitor in the equivalent circuit can be replaced by a so-called constant phase element (CPE) that is a frequency-dependent element and related to surface roughness¹⁵.

The impedance function of a CPE has the following equation

$$Z_{CPE} = 1/(Y_0 \omega)^n \tag{4}$$

where the amplitude Y_0 and n are frequency independent, and ω is the angular frequency for which $-Z''$ reaches its maximum values, n is dependent on the surface morphology, with values, $-1 \leq n \leq 1$. Y_0 and n can be calculated by the equations proved by Mansfeld *et al*¹¹.

An equivalent circuit consisting of nine elements depicted to interpret the measured impedance data of the aluminum in hydrochloric acid medium. They are shown in Figure 3(b).

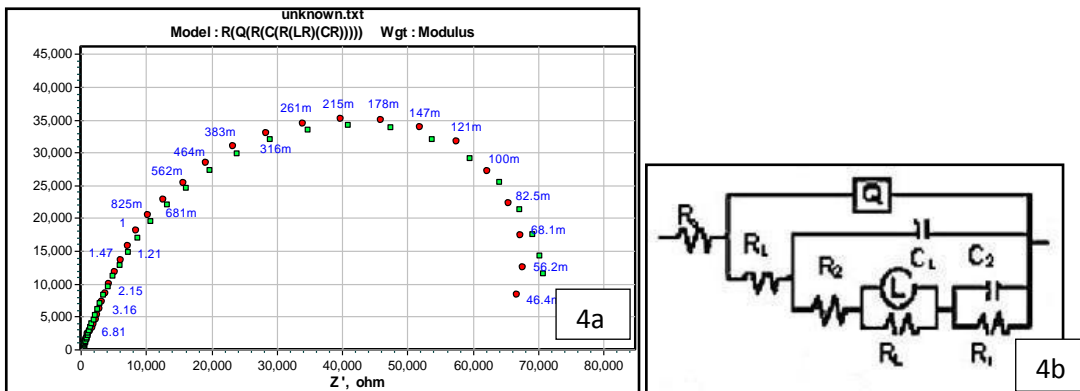


Figure 3: (a) Equivalent circuit used to fit the experimental EIS data for the corrosion of aluminum in HCl of pH=3 containing APPE (0.4gL⁻¹) at 30 °C. (b) Equivalent circuit.

In these equivalent circuits R_s is the solution resistance and R_t is the charge transfer resistance. R_L and L represent the inductive elements. CPE (Q) is constant phase element in parallel to the series capacitors C_1 , C_2 and series resistors R_1 , R_2 , R_L and R_t . R_L is parallel with the inductor L .

The double layer capacitance (C_{dl}) was calculated from equation (5)

$$C_{dl} = C_1 + C_2 \tag{5}$$

Polarization resistance (R_p) was calculated using the equation (6)

$$R_p = R_L + R_t + R_1 + R_2 \tag{6}$$

Since polarization resistance (R_p) is inversely proportional to the corrosion current and it can be used to calculate the percentage inhibition efficiency (%I.E.) using the relation (7)

$$I. E. \% = \frac{R_{p(inh.)} - R_p}{R_{p(inh.)}} \times 100 \tag{7}$$

where $R_{p(inh.)}$ and R_p are the polarization resistances in the presence and absence of inhibitor.

As seen from Figure 2, solution resistance (R_s) remained almost constant, with and without the addition of APPE for aluminum. It was also observed that the value of constant phase element (Q), decreased, while the values of charge transfer resistance (R_t) increased with increasing concentration of inhibitor. This observation indicates that the inhibition efficiency increases with the increase in concentration of APPE.

The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of inhibitor molecules on the aluminum surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the surface. The decrease in this capacity with increase in inhibitor concentrations may be attributed to the formation of a protective layer on

the electrode surface. The thickness of this protective layer increased with increase in inhibitor concentration up to their critical concentration of 0.4g L⁻¹ and then decreased. The obtained CPE (Q) values decreased noticeably with increase in the concentrations of inhibitor. This may be due to the adsorption of constituents of APPE on the metal surface as Q is inversely proportional to the thickness of the protective layer¹⁵.

The impedance parameters derived from Nyquist plot and inhibition efficiency of APPE in hydrochloric acid medium are given in Table 2. The measured value of polarization resistance was found to increase with the increasing concentrations of APPE. It may be due to the decrease in the corrosion rate for the aluminum with increase in inhibitor concentration. This is in accordance with the observations obtained from potentiodynamic measurements.

3. Effect of temperature

Inhibition efficiency of the APPE decreased with increase in temperature. This can be attributed to the decrease in the protective nature of the inhibitive film formed on the metal surface (or desorption of the inhibitor molecules from the metal surface) at higher temperatures¹¹. This suggests physical adsorption mechanism (11–13). However, at higher concentrations of inhibitor this decrease was small. The study of effect of temperature was used to calculate energy of activation (E_a) for the corrosion process in the presence and absence of inhibitor using Arrhenius rate law Equation (8)¹¹.

$$\ln CR = B - \frac{E_a}{RT} \tag{8}$$

where B is a constant which depends on the metal type and R is the universal gas constant (R= 8.314 J mol⁻¹K⁻¹) T is the absolute temperature. Plots of ln (CR) versus 1/T gave straight lines with slope (slope = -E_a/R.).The Arrhenius plot for the corrosion of aluminum in hydrochloric acid medium of pH=3 in the absence and in the presence of inhibitor is shown in Figure 4. The values of enthalpy of activation (ΔH_a) and entropy of activation (ΔS_a) for corrosion and inhibition process were calculated from transition state equation (9)¹¹.

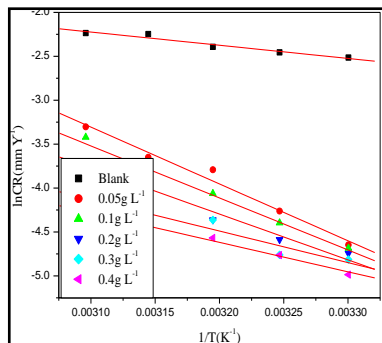


Figure 4: Arrhenius plot for the corrosion of aluminum containing different concentrations of APPE. in HCl of pH=3

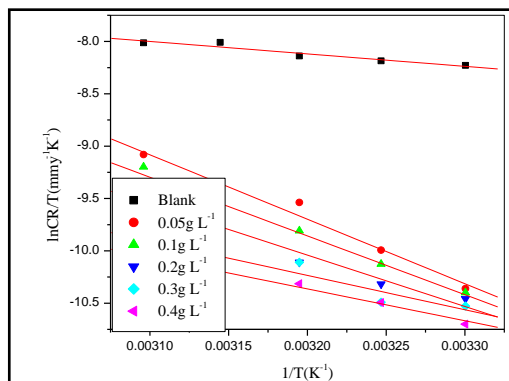


Figure 5: Plot of ln(CR/T) vs 1/T for the corrosion of aluminum in HCl of pH=3 containing different concentrations of APPE.

$$CR = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (9)$$

where h is Plank's constant ($h = 6.626 \times 10^{-34}$ Js) and N is Avogadro's number ($N = 6.023 \times 10^{23}$)

Plot of $\ln(CR/T)$ versus $1/T$ for the corrosion of aluminum in hydrochloric acid medium containing different concentrations of APPE is shown in Figure 5. Plot of $\ln(CR/T)$ versus $1/T$ gave straight lines with slope = $-\Delta H_a/R$, Intercept = $\ln R/Nh + \Delta S_a/R$. Results are tabulated in Table 3.

Table 3: Activation parameters for the corrosion of aluminum in hydrochloric acid medium of pH=3 containing different concentrations of APPE.

[APPE] (g L ⁻¹)	E _a (kJmol ⁻¹)	ΔH _a (kJmol ⁻¹)	ΔS _a (kJ mol ⁻¹ K ⁻¹)
0.0	12.49	9.89	- 161.69
0.05	77.48	74.88	- 234.78
0.1	67.16	64.55	- 324.96
0.2	32.82	30.21	-211.64
0.3	16.51	13.91	-158.25
0.4	22.09	19.49	-173.42

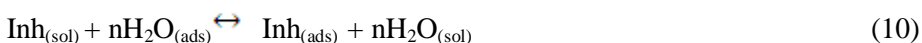
As reported in Table 3, energy of activation (E_a) values increased significantly after the addition of inhibitor. Increase in the energy of activation (E_a) values, with increasing inhibitor concentrations indicate the increase in energy barrier for the corrosion reaction¹³. The adsorption of the inhibitor molecules on the surface of the aluminum blocks the charge transfer during corrosion reaction, thereby increasing the activation energy¹².

The enthalpy of activation (ΔH_a) also something as energy of activation was more in the presence of inhibitor than in the absence of inhibitor on aluminum in hydrochloric acid and sulfuric acid media. This may be due to the adsorption of inhibitor molecules on the metal surface. The enthalpy of activation (ΔH_a) was positive. This may be due to the endothermic nature of the aluminum dissolution in both the acid media and the dissolution of the metal is difficult¹¹.

The values of entropy of activation (ΔS_a) were higher for inhibited solutions than those for the uninhibited solutions. This suggested that an decrease in randomness occurred on going from reactants to the activated complex. This might be the results of the adsorption of organic compound present in the APPE from the acidic solution which could be regarded as a quasi-substitution process between the organic compound in the aqueous phase and water molecules at electrode surface. In this situation, the adsorption of inhibitor is accompanied by desorption of water molecules from the surface. Thus the increase in entropy of activation (ΔS_a) was attributed to the increase in solvent entropy¹¹⁻¹³.

4. Adsorption considerations

The adsorption route is usually regarded as a substitution process between the inhibitor in the aqueous solution [Inh(sol)] and water molecules adsorbed at the metal surface [H₂O_(ads)] as given in reaction^{10,13}.



where n represents the number of water molecules replaced by one molecule of adsorbed inhibitor. The adsorption bond strength is dependent on the composition of the metal, corrodent, inhibitor structure, concentration and orientation as well as temperature. Adsorption isotherms are usually employed to explain the mechanism of interaction between an inhibitor (adsorbate) and an adsorbent surface. This is usually achieved by fitting the degree of surface coverage data into various adsorption isotherms or models and the correlation coefficients (highest) is used to determine the best fit isotherm which can then be used to describe the inhibitor adsorption mechanism. In this work, the best fit isotherm was the Langmuir adsorption model which relates the degree of surface coverage (θ) to the concentration of the extracts (C_{inh.}) according to equation (11).

$$\frac{\theta}{1 - \theta} = K_{ads} \cdot C \tag{11}$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process and C is the inhibitor concentration, and θ is the degree of the surface coverage, which was calculated using equation (3). This model has also been used for other inhibitor systems¹⁸. With hydrochloric acid plots of C_{inh}/θ versus C_{inh} gave straight lines with intercept (intercept = $1/K$). Langmuir adsorption isotherms are as shown in Figure 6.

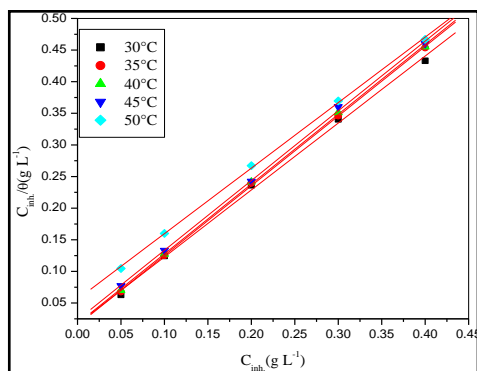


Figure 6: Langmuir adsorption isotherms for the adsorption of APPE on aluminum in HCl of pH=3

The correlation coefficient (R^2) was used to choose the isotherm that best fit the experimental data. The linear regression coefficients were close to unity, and the slopes of straight lines were nearly unity, suggested that the adsorption of organic compounds present in APPE obeyed Langmuir’s adsorption isotherm, and there is negligible interaction between the adsorbed molecules¹⁸.

Adsorption / desorption constant (K) is related to standard free energy of adsorption

(ΔG°_{ads}) by the relation (12).

$$K = \frac{1}{C_{water}} \exp. \left[\frac{\Delta G^{\circ}_{ads}}{RT} \right] \tag{12}$$

where C_{water} is the concentration of water in solution expressed in $g L^{-1}$, R is the universal gas constant ($8.314 J mol^{-1} K^{-1}$) and T is the absolute temperature. It must be noted that the concentration unit of water molecules has to be same as that of the inhibitor (the unit of C_{water} is $g.L^{-1}$ with the value of approximate 1×10^3), and the calculated free energy of adsorption (ΔG°_{ads}) values (at different temperatures) obtained for hydrochloric acid medium of pH=3 are listed in Table 4¹¹.

Table 4: Thermodynamic parameters for the adsorption of APPE on aluminum in in hydrochloric acid of pH=3

Temp. (K)	ΔG°_{ads} (kJmol ⁻¹)	ΔH°_{ads} (kJmol ⁻¹)	ΔS°_{ads} (kJmol ⁻¹ K ⁻¹)
303	-30.23	-77.05	-0.154
308	-29.94		
313	-28.49		
318	-28.42		
323	-27.14		

Negative values of free energy of adsorption (ΔG°_{ads}) suggest the spontaneous adsorption of inhibitor on the surface of metal and the stability of the adsorbed layer on the aluminum.

Plot of ΔG°_{ads} versus T was used to calculate the standard enthalpy of adsorption (ΔH°_{ads}) and the standard entropy of (ΔS°_{ads}) according to the thermodynamic equation (13).

$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T\Delta S_{ads}^{\circ} \quad (13)$$

Plot of ΔG_{ads}° versus T for aluminum in hydrochloric acid medium of pH=3 is shown in Figures 7. Figure 7 clearly shows the dependence of ΔG_{ads}° on T which indicates good correlation among thermodynamic parameters. The thermodynamic parameters obtained for aluminum in hydrochloric acid medium of pH=3 are tabulated in Table 4.

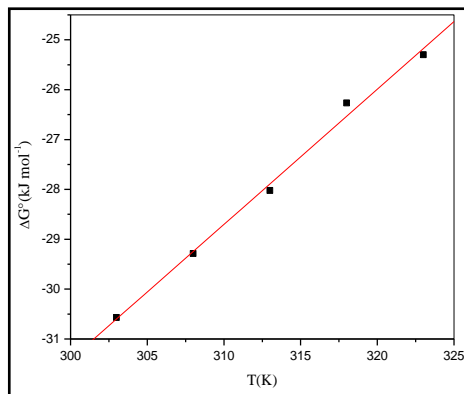


Figure 7: Plot of ΔG_{ads}° versus T for the adsorption of APPE on aluminum in HCl of pH=3

In general, standard free energy of adsorption (ΔG_{ads}°) values of adsorption of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, resulting in physisorption. Standard free energy of adsorption (ΔG_{ads}°) values of -40 kJ mol^{-1} or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, resulting in chemisorption¹⁸.

The values of standard free energy of adsorption (ΔG_{ads}°) for the adsorption of APPE on the aluminum surface in studied concentrations of hydrochloric acid medium of pH=3 was more than -20 kJ mol^{-1} and less than -40 kJ mol^{-1} which indicates the adsorption of constituents of APPE on the surface of aluminum could be due to both the process¹⁸.

While an endothermic adsorption process ($\Delta H_{ads}^{\circ} > 0$) is attributed unequivocally to chemisorption, an exothermic adsorption process ($\Delta H_{ads}^{\circ} < 0$) may involve either physisorption or chemisorption or a mixture of both the processes. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of adsorption enthalpy. According to the reported literature, for physisorption process enthalpy of adsorption is lower than $41.86 \text{ kJ mol}^{-1}$, and for chemisorption process the value approaches 100 kJ mol^{-1} ⁽¹⁸⁾.

In the present investigation with APPE as inhibitor, the calculated values of enthalpy of adsorption (ΔH_{ads}°) is $-77.05 \text{ kJ mol}^{-1}$ in hydrochloric acid medium of pH=3. This suggests the adsorption of APPE on the surface of aluminum are mixture of both processes. The entropy of adsorption (ΔS_{ads}°) value is negative, indicating that an ordering takes place when the inhibitor gets adsorbed on the metal surface.

5. Mechanism of corrosion and inhibition process

APPE is composed of numerous natural organic heterocyclic compounds. Major constituents of the aqueous extract of *Andrographis paniculata* plants are reported to be lactone andrographolide, 5,7,2¹,3¹-tetramethoxy flavanone and 5-hydroxy 7, 2¹,3¹- trimethoxy flavanone. The structures of the same are given in Figures 8(a), 8(b) and 8(c) respectively.

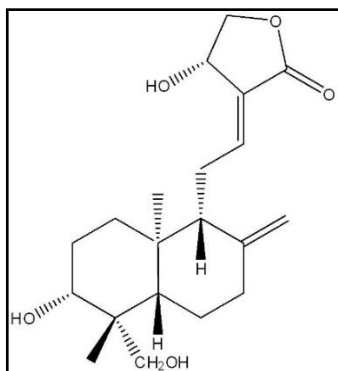


Figure8 (a): Structure of Lactone Andrographolide

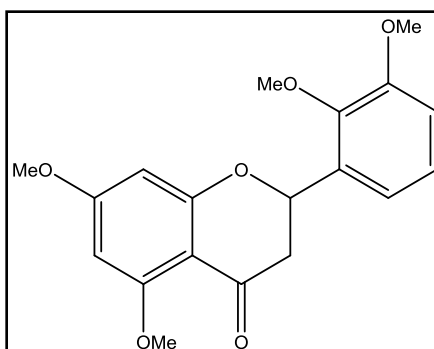


Figure8 (b): Structure of 5,7,2',3'- tetramethoxy flavanone

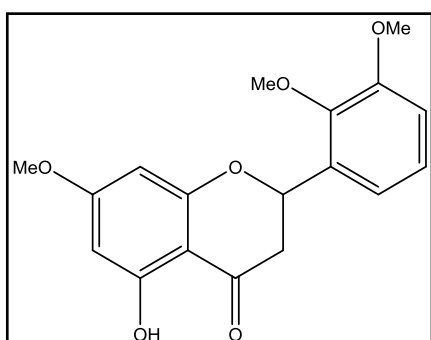


Figure 8(c): Structure of 5-hydroxy 7, 2',3'- trimethoxy flavanone.

The presence of these compounds are confirmed by taking the I.R. spectrum of APPE. Figure 9 shows the FTIR spectrum of APPE. Absorption at 3446 cm^{-1} can be assigned to stretching frequency of O–H. The peak at 2929 cm^{-1} can be assigned to stretching frequency of aromatic group. The 1749 cm^{-1} band is assigned to the stretching frequency of C=O group. The adsorption band at 1604 cm^{-1} is assigned to the stretching frequency of cyclic ketone group.

Surface of aluminum is covered with thin layer of α alumina which initially thickens on exposure to neutral aqueous solution with the formation of a layer of crystalline hydrated alumina. The aluminum surface has positive charge when in an acidic environment (in contact with hydrochloric acid). The mechanism of adsorption can be predicted on the basis of the mechanism proposed for the corrosion of aluminum in hydrochloric acid.

Anodic reactions



Cathodic reactions



Two modes of adsorption process could be suggested to explain the inhibitory action of APPE for the corrosion of aluminum in hydrochloric acid medium. In aqueous acidic solution, lactone andrographolide, 5,7,2',3'-tetramethoxy flavanone and 5-hydroxy 7, 2',3'- trimethoxy flavanone molecules may exist either as unprotonated molecule or in the form of protonated species.

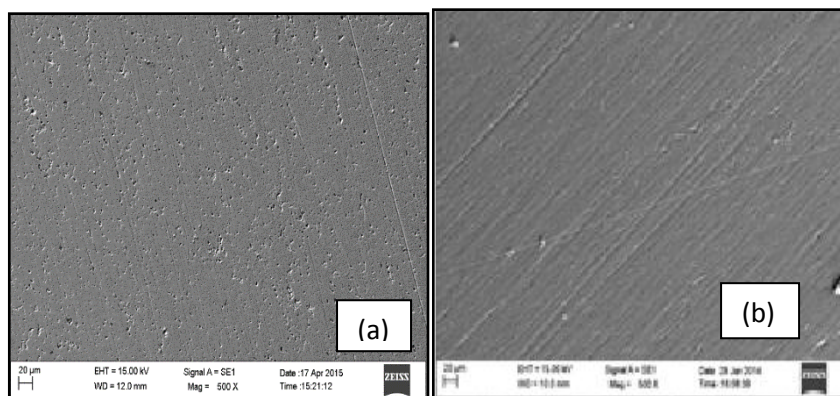


Figure 9: SEM images of aluminum in (a) 0.001 M HCl and (b) 0.001M HCl + APPE (0.4gL⁻¹)

APPE acts as an anodic type at lower concentrations of inhibitor, and brings down anodic reactions under control. In acid medium, aluminum is positively charged since the pH of the potential of zero charge for aluminum at the oxide/solution interface is 9.0–9.1. This will attract negative chloride ions from the solution, and these ions will get adsorbed on the surface of the metal. In acidic solution the hydroxyl groups of lactone andrographilide and cyclic ketone and methoxy groups of 5,7,2¹,3¹-tetramethoxy flavanone and 5-hydroxy 7, 2¹,3¹-trimethoxy flavanone present in APPE can be easily protonated because of their high electron density. The protonated molecules are attracted to the anionic layer which is formed on the metal surface, and get physically adsorbed on the same. This will result in the formation of protective barrier on the surface of the metal. This barrier will prevent the further dissolution of the metal and prevent the metal from undergoing corrosion. Enhanced corrosion inhibition may be also due to the π electrons of the double bond of constituents of the extract which also acts as high electron rich centers¹⁹.

As the inhibitor concentrations increased, the rate of adsorption of inhibitor molecules on the metal surface increased. These adsorbed molecules have larger size hence, they cover the entire metal surface and form a protective film, thereby bring down both anodic and cathodic reactions under control and hence acts as mixed inhibitor with preferentially decreasing the rate of anodic reactions. In these type of adsorption the force of attraction between the inhibitor and metal surface may be electrostatic. The unprotonated lactone andrographilide, 5,7,2¹,3¹-tetramethoxy flavanone and 5-hydroxy 7,2¹,3¹- trimethoxy flavanone molecules present in APPE may be chemisorbed on the metal surface on the basis of donor–acceptor interactions between π -electrons of double bonds in alkene and aromatic rings and vacant p-orbitals of Al. These chemisorbed molecules decreases the rate of both anodic and cathodic reactions and hence acts as mixed type of inhibitor²⁰.

5. Surface morphology studies: SEM and EDX analysis

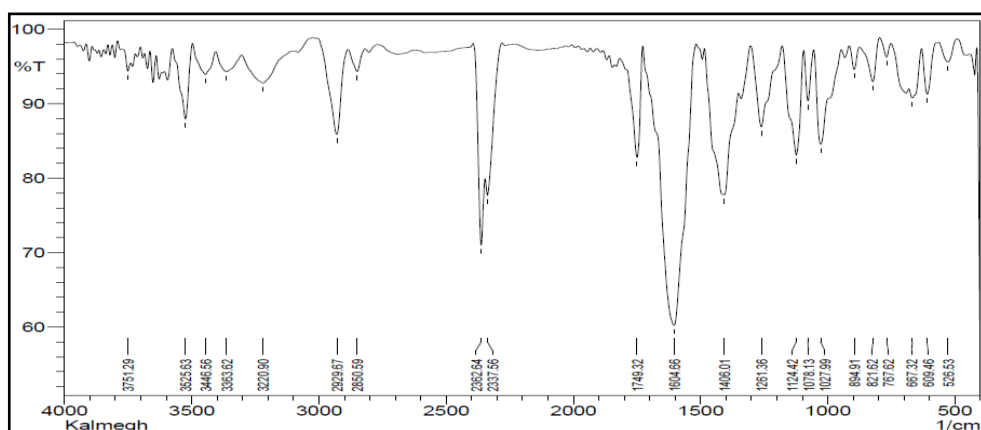


Figure 10: IR spectrum of solid residue of APPE.

The SEM images of aluminum in hydrochloric acid medium of pH=3 in the absence and presence of inhibitor are shown in Figures 10(a) and 10(b) respectively. The SEM image of aluminum in hydrochloric acid medium of pH=3 showed the heterogeneous surface with small pits, which indicates that the metal undergoes pitting corrosion in hydrochloric acid medium¹⁹. The SEM image of aluminum after the addition of APPE

(0.4gL⁻¹) to hydrochloric acid medium of pH=3 showed the decrease in the number of pits and increase in the smoothness of the surface. That is due to the adsorption of constituents of APPE on the surface of aluminum decreases the rate of corrosion.

Interaction of corrosive with metal and the adsorption of inhibitor on its surface was confirmed by EDX analysis. Results are tabulated in Table 5. In the presence of inhibitor small peak for chlorine indicates the interaction of the medium with metal and peak due to carbon is due to the adsorption of inhibitor molecule.

Table 5: Results of EDX analysis for corrosion inhibition of aluminum using APPE (0.4 g L⁻¹) in hydrochloric acid of pH=3

Medium	Composition(%)				
	Al	O	Si	Cl	C
Aluminum in HCl	92.31	7.16	0.37	0.16	–
Aluminum in HCl +APPE(0.4gL ⁻¹)	74.82	4.43	0.20	0.04	20.52

Conclusions

- The inhibition efficiency of APPE increases with increase in its concentration and decreases with increase in temperature.
- APPE functions as anodic type at lower concentrations of inhibitor and mixed type at higher concentrations of inhibitor.
- APPE gets adsorbed on the aluminum surface via both physisorption and chemisorption and follows Langmuir's adsorption model.
- **APPE**, may be considered as an effective ecofriendly green inhibitor for the corrosion control of aluminum in hydrochloric acid medium.

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