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## RESEARCH LETTER

### Leaves extract of *Ananas sativum* as green corrosion inhibitor for aluminium in hydrochloric acid solutions

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The inhibition of corrosion of aluminum in hydrochloric acid solutions by the ethanolic extract of the leaves of *Ananas sativum* was studied using weight loss and hydrogen evolution methods. It was found that the plant extract retarded the acid induced corrosion of aluminum. Inhibition efficiency increased with increasing concentration of the extract and temperature. Adsorption studies revealed that Langmuir adsorption isotherm is the best adsorption model applicable to the adsorption of *A. sativum* on aluminum surface. Activation parameters such as activation energies ( $E_a$ ), activation enthalpy ( $\Delta H^\circ$ ), and activation entropy ( $\Delta S^\circ$ ) were evaluated from the effect of temperature on the corrosion and inhibition processes.

**Keywords:** *Ananas sativum*; aluminum; corrosion inhibition; adsorption; Langmuir; acid

#### Introduction

The protection of metals against corrosion has attracted much attention globally as a result of huge losses of natural resources and finances that are sustained annually all over the world due to corrosion. The most important feature of aluminum is its corrosion resistance due to the presence of a thin, adherent, and protective surface oxide film. Because of this advantage, aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, machinery, and chemical batteries (1–3).

However, when exposed to aggressive environments, such as the use of acid solutions for pickling, chemical and electrochemical etching of aluminum, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling, these processes usually lead to substantial loss of the metal due to corrosion. Inhibitors are used to prevent metal dissolution and minimize acid consumption. Most of the efficient acid inhibitors are organic compounds that contain mainly nitrogen, sulfur or oxygen atoms in their structure (4–6). Despite the large number of organic inhibitors confirmed to be suitable for Al corrosion, there is always a need for developing new organic corrosion inhibitors. Besides, most of these inhibitors are toxic to the environment implying that their use may solve corrosion problem but enhance environmental problems.

The study of plant extracts as low-cost and eco-friendly corrosion inhibitors is of great interest from an environmental perspective and is attracting a significant level of attention. Green corrosion inhibitors have a promising future for the quality of the environment because they do not contain heavy metals or other toxic compounds. In addition, they are biodegradable and renewable source of materials.

Some reports have been highlighted on the successful application of plant extracts as corrosion inhibitors for aluminum in different media. The inhibitive action of the acid extracts of seeds, leaves, and bark from the *Ficus virens* plant toward the corrosion of aluminum in hydrochloric and sulfuric acids has been studied by Jain et al. (7). The use of aqueous solution of garlic in controlling the corrosion of Al immersed in NaOH solution has been reported (8). Application of the extract of different parts of Peepal (*Ficus religiosa*) as inhibitors for the corrosion of aluminum in HCl has been studied (9). Ebenso et al. (10) reported that the ethanolic extract of *Carica papaya* and *Azadirachta indica* are good inhibitors for Al corrosion in acidic medium. The inhibitive action of the mucilage extracted from the modified stems of *Opuntia* extract toward the acid corrosion of Al has been reported by El-Etre (11). The inhibitive action of extract of tobacco plant toward the corrosion of steel and aluminum has been investigated (12). Kliskic et al. (13) reported aqueous

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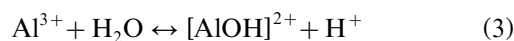
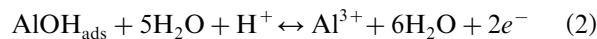
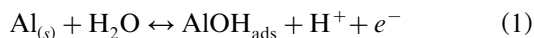
extract of *Romarinus officinalis* as a good inhibitor for the corrosion of Al–Mg alloy in chloride solution. Oguzie found that extract of *Occimum basislicum* (14) has the potential of inhibiting the corrosion of aluminum in acidic and alkaline media and *Sansevieria trifasciata* in alkaline medium (15). Leaves and seed extract of *Gossypium hissutum* L. (16) and *Phyllanthus amarus* (17) as effective corrosion inhibitors for aluminum in NaOH as well as *Delonix regia* (18) in acidic media has been reported by Abiola and coworkers. El-Hosary et al. studied the corrosion inhibition of aluminum and zinc in HCl by *Hibiscus sabdariffa* extract (19). In a related study, Noor (20) reported the corrosion inhibitive effect of the leaves extract of the same plant for aluminum in alkaline solutions. Inhibition of aluminum corrosion in NaOH by *Ambrosia maritime* (damsissa) has been reported by Addel-Gaber et al. (21). Obot and Obi-Egbedi (22) investigated the potential of *Ipomoea involcrata* in inhibiting corrosion of aluminum in NaOH. Other naturally occurring substances reported as effective corrosion inhibitor for aluminum also include aqueous extracts of some seed, leaves, fruits, and fruit peels in NaOH (23).

Series of reports have been highlighted in our laboratory on naturally occurring substances and plant extracts as green corrosion inhibitors. These include gum Arabic in inhibiting aluminum corrosion in alkaline medium (24), for mild steel and aluminum in acidic medium (25), *Raphia hookeri* exudates gum for mild steel and aluminum in acidic environment (26,27), *Vigna unguiculata* for aluminum in acidic and alkaline media (28), exudates gums from *Pachylobus edulis* (29) and *Dacrodyes edulis* (30) for aluminum in HCl. The encouraging results obtained from previous studies and as part of our contribution to the growing interest on environmentally friendly corrosion inhibitors, the present work reports on the corrosion inhibitive properties of *Ananas sativum* for aluminum corrosion in acidic solutions using weight loss and hydrogen evolution methods at 303–333 K. *A. sativum* is a tropical fruit common in Nigeria and other African countries. The leaf of the plant is biodegradable and a renewable material.

## Results and discussion

### Corrosion inhibitive effect by *Ananas sativum* extract

The general mechanism for the corrosion of Al in acidic medium has been reported by Nugen and Foley as follows (31):



The controlling step in the metal dissolution is the complexation reaction between the hydrated cation and the anion present (Equation (4)). In the presence of chloride ions, the reaction will correspond to:



The soluble complex ion formed leads to the dissolution of the metal.

The corrosion of aluminum in 0.1 M HCl in the absence and presence of different concentrations of *A. sativum* in the temperature range 303–333 K was studied using weight loss technique. Figure 1 shows plots of weight loss against time for Al corrosion in the blank (0.1 M HCl) and in the presence of different concentrations of *A. sativum* extract at (a) 303 and (b) 333 K corresponding to the lowest and highest temperatures studied, respectively. From the plot, it is seen that at a given temperature the weight

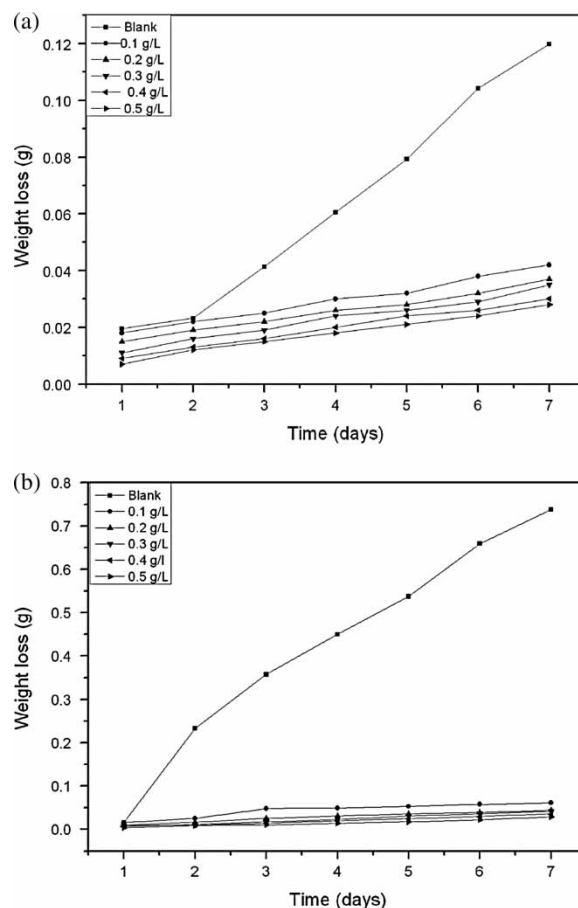


Figure 1. Variation of weight loss against time for aluminum corrosion in 0.1 M HCl in the presence of different concentrations of extract at (a) 303 and (b) 333 K.

loss of Al increases as the period of immersion increased both in the absence and presence of the inhibitor indicating that the rate of corrosion of Al increases with time. Also the weight loss of Al is observed to increase with increase in temperature both in the blank solution and in the solution containing different concentrations of *A. sativum*. These observations imply that the corrosion of Al in HCl is influenced by immersion time, concentration of *A. sativum* and temperature.

From the plot, weight loss for systems containing *A. sativum* was found to be lower compared to the blank indicating that different concentrations of *A. sativum* retard the corrosion of Al in 0.1 M HCl. The figure reveals that the inhibitor (plant extract) actually inhibited the HCl induced corrosion of aluminum to an appreciable extent. The figure also reveals that aluminum corrosion by HCl occurs not by simple homogenous process but by a heterogeneous one consisting of different or same rates. This assertion is made from the non-uniformity or non-linearity of the plots obtained (32).

The calculated values of corrosion rate (mpy) and inhibition efficiency (I%) for aluminum corrosion in 0.1 M HCl in the presence of different concentration of the plant extract from the weight loss measurements are shown in Table 1. Results presented in the table indicate that corrosion rate of aluminum in the acid medium was reduced in the presence of *A. sativum* extract compared to the blank solution. This is an indication that the extract inhibited acid induced corrosion of aluminum. It is also seen in the table that corrosion rate of Al in the presence of the extract decreases with increase in the extract concentration. Corrosion rate is also observed to increase with rise in temperature. Inhibition efficiency values were found to increase with increase in concentration of *A. sativum* and temperature. Maximum inhibition efficiency of 96.09% was obtained with extract concentration of 0.5 g/L at 333 K. Increase in inhibition efficiency with increase in temperature is

suggestive of chemisorption of the *A. sativum* components onto the aluminum surface.

Inhibition of Al corrosion in 0.1 M HCl in the presence of the crude extract could be attributed to the adsorption of the phytochemical constituents of the extract on the aluminum surface which creates a barrier isolating the metal from the aggressive anions present in solution thus reducing the corrosion process. The results of the preliminary phytochemical screening reveal the crude extract contain alkaloids, tannins, cardiac glycosides, and saponins. These substances contain oxygen and nitrogen atoms in their molecules which are regarded as centers of adsorption. The adsorption of these compounds on the aluminum surface makes a barrier for mass and charge transfers. Consequently, the metal is protected from the aggressive anions of the acid. The degree of protection increases with increase in extract concentration due to higher degree of surface coverage resulting from enhanced inhibitor adsorption. One of the major drawbacks of the use of plant extract as corrosion inhibitors is the inability to pinpoint the major active component that is responsible for the inhibiting action owing to the complex chemical composition of the crude extract. However, further investigation and the use of surface analytical techniques will enable the characterization of the active materials in the adsorbed layer and assist in identifying the most active ingredients which is currently being pursued in our laboratory.

#### Hydrogen evolution method

The inhibitive effect of *A. sativum* ethanolic extract on the corrosion of aluminum in HCl at a temperature of 303 K was also investigated using hydrogen evolution technique. This technique provides a rapid and sensitive means for gauging any interruption by an inhibitor with regard to gas evolution at the metal-corroderent interphase. Results obtained by this technique are corroborated by other well-established methods including weight loss and thermometry

Table 1. Calculated values of corrosion rates (mpy) and inhibition efficiency (I%) for aluminum corrosion in 0.1 M HCl in the absence and presence of different concentrations of extract at different temperatures from weight loss measurements.

Systems/concentrations	Corrosion rate (mpy) $\times 10^{-3}$				Inhibition efficiency (I%)			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank (0.1 M HCl)	15.20	26.92	74.30	93.45	—	—	—	—
0.1 g/L extract	3.67	4.33	7.46	7.75	75.86	83.92	89.96	94.71
0.2 g/L extract	2.29	2.88	5.04	5.60	84.93	89.30	93.22	94.01
0.3 g/L extract	1.50	2.12	4.16	5.30	90.13	92.12	94.40	94.33
0.4 g/L extract	1.32	1.90	4.12	4.50	91.32	92.94	94.95	95.19
0.5 g/L extract	1.13	1.39	3.55	3.66	92.53	94.84	95.22	96.09

(11,33), potentiostatic polarization (34), and impedance spectroscopy (35). Figure 2 is a typical plot showing the variation of volume of  $H_2$  gas evolved with time for 2 M HCl without and with different concentrations of the inhibitor (extract) at 303 K. The plots reveal slow rates of hydrogen evolution at the start of the reaction and after an incubation period, which correspond to the time interval needed by the corrodent to break down the pre-immersion oxide film on the aluminum surface, the volume of evolved  $H_2$  gas varies linearly with reaction time. It is also observed from the plots that the volume of hydrogen evolved was reduced on introduction of the extract onto the blank corrodent compared to the free acid and further decreases as the concentration of the extract increases.

Corrosion rate and inhibition efficiency values for aluminum in 2 M HCl in the absence and presence of varying concentrations of the extract at 303 K from the hydrogen evolution measurements are given in Table 2. From the table, it is seen that the value of corrosion rate was high in the blank acid solution in the absence of the inhibitor. Addition of the plant extract to the acid solution led to a substantial reduction in the corrosion rate of aluminum and was found to decrease as the extract concentration increases. Inhibition efficiency and surface coverage increases with increase in concentration of the extract. Similar trend was observed for the weight loss techniques also employed in the present study.

### Adsorption studies

One possible mechanism for corrosion inhibition using organic compounds is the adsorption of the

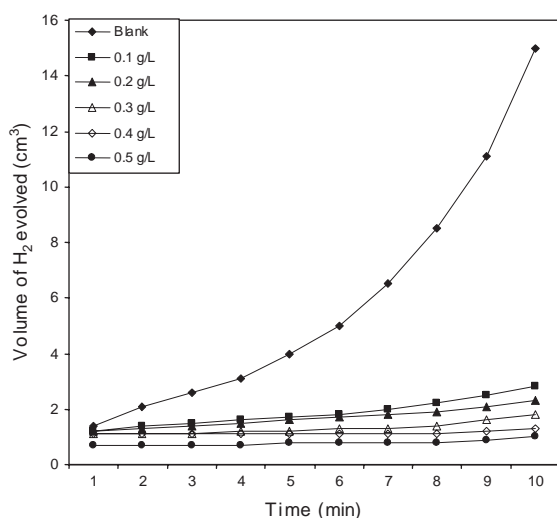


Figure 2. Variation of volume of  $H_2$  evolved against time for aluminum, corrosion in 2 M HCl in the absence and presence of different concentrations of extract at 303 K.

Table 2. Calculated values of corrosion rate and inhibition efficiency for aluminum corrosion in 2 M HCl containing different concentrations of extract at 303 K from hydrogen evolution measurements.

Systems/ concentrations	Corrosion rate (mL/min)	Inhibition efficiency (I%)
Blank (2 M HCl)	75.0	—
0.1 g/L extract	14.0	81.13
0.2 g/L extract	11.5	84.46
0.3 g/L extract	9.0	87.78
0.4 g/L extract	6.5	91.11
0.5 g/L extract	5.0	93.10

inhibitor which blocks the metal surface and thus do not permit the corrosion to take place. The adsorption provides the information about the interaction among the adsorbed molecules themselves as well as their interaction with the metal surface (36). Two main types of interaction can describe the adsorption of organic compounds namely: physical adsorption and chemical adsorption. These are dependent on the electronic structure of the metal, the nature of the electrolyte, and the chemical structure of the inhibitor. Adsorption isotherms are very important to understand the mechanism of heterogeneous organo-electrochemical reactions (37) involving solid surfaces. In discussing adsorption isotherms, the degree of surface coverage ( $\theta$ ) is very useful. The degree of surface coverage values for different concentrations of *A. sativum* from the weight loss measurements obtained using  $\theta = I\%/100$  assuming a direct relationship between surface coverage and inhibition efficiency were fitted into the most frequently used adsorption isotherms namely: Temkin, Frumkin, Langmuir, Freundlich, Hill de Boer, Parsons, Flory Huggins, Dhar-Flory Huggins, and Bockris Swinkles; and the correlation coefficients ( $R^2$ ) were used to determine the best fitted isotherm. All of these isotherms are of the general form (38):

$$f(\theta, x) \exp(-2a\theta) = KC, \quad (6)$$

where  $f(\theta, x)$  is the configurational factor which depends upon the physical model and assumption underlying the derivative of the isotherm (38),  $\theta$  is the surface coverage,  $C$  is the inhibitor concentration,  $x$  is the size ratio,  $a$  is the molecular interaction parameter, and  $K$  is the equilibrium constant of adsorption process.

The usefulness of  $\theta$  values in explaining the best isotherm to determining the adsorption process has shown that the experimental data obtained in this study fits well into Langmuir adsorption isotherm formulated as:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C. \quad (7)$$

$K$  is related to the free energy of adsorption by the equation:

$$K = \frac{1}{55.5} \exp \left[ \frac{-\Delta G_{\text{ads}}^{\circ}}{RT} \right], \quad (8)$$

where  $\theta$  is the degree of surface coverage,  $K_{\text{ads}}$  is the equilibrium constant of adsorption process, and  $\Delta G_{\text{ads}}^{\circ}$  is the free energy of adsorption values. Plot of  $C/\theta$  against  $C$  as shown in Figure 3 gave straight lines which clearly show that aluminum corrosion inhibition in HCl by *A. sativum* extract at the temperatures studied obeys Langmuir adsorption isotherm. The correlation coefficient, slopes, and adsorption coefficients obtained from Langmuir isotherm plots are shown in Table 3. The values of correlation coefficient as shown in the table are quite good; an indication that the experimental data obtained in this study and hence adsorption of *A. sativum* extracts onto aluminum surface follows Langmuir isotherm. The values of  $K$  revealed that adsorption coefficient increases with increase in temperature. This is an indication that adsorption and hence inhibition efficiency increases with rise in temperature. Generally,  $K$  denotes the strength between adsorbate and adsorbent. Large values of  $K$  imply more efficient adsorption and hence better inhibition efficiency (39). Higher value of  $K$  at 333 K implies that more *A. sativum* extract was adsorbed onto aluminum surface leading to greater surface coverage and hence better protection efficiency than at 303 K. The Langmuir isotherm characterizes chemisorption of the adsorbed species and postulates monolayer adsorption of the adsorbate onto the adsorbent which is expected to have a slope of unity. This is clearly demonstrated in

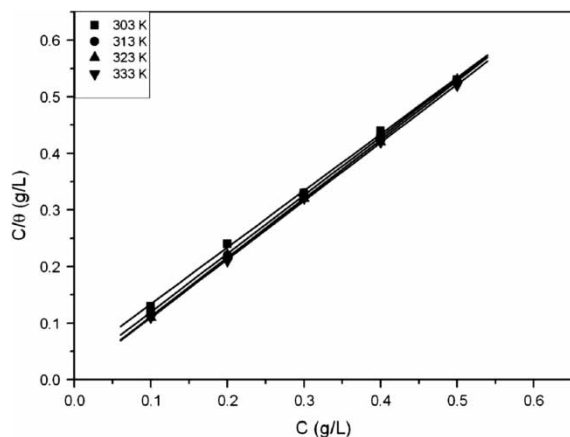


Figure 3. Langmuir adsorption isotherm plot for aluminum corrosion in 0.1 M HCl for *A. sativum* extract at different temperatures.

this study. The slope of unity obtained in this study is an indication that the adsorption of the extract components is approximated by Langmuir adsorption isotherm and that monolayer of the inhibitor species must have been attached to aluminum surface without lateral interaction between the adsorbed species (40).

The free energy of adsorption values,  $\Delta G_{\text{ads}}^{\circ}$ , was obtained from Equation (3). The values obtained are presented in Table 3. Results presented in the table indicate that the values of  $\Delta G_{\text{ads}}^{\circ}$  are negative in all cases and ranged between  $-18.64$  and  $-24.86$  kJ/mol. The negative values indicate a spontaneous adsorption of the inhibitor molecules. The values of  $\Delta G_{\text{ads}}^{\circ}$  are below  $-40$  kJ/mol which indicate that the inhibitor function by physically adsorbing on the surface of the metal. Generally, values of  $\Delta G_{\text{ads}}^{\circ}$  up to  $-20$  kJ/mol are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption) while those more negative than  $-40$  kJ/mol involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorption) (32). Physical adsorption is a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. Adsorption of negatively charged species is facilitated if the metal is positively charged. Positively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions adsorbed on the metal surface.

Results of the present study have shown that *A. sativum* extract inhibits the acid induced corrosion of aluminum by virtue of adsorption of its components onto the metal surface. The inhibition process is a function of the metal, inhibitor concentration, and temperature as well as inhibitor adsorption abilities which is so much dependent on the number of adsorption sites. The mode of adsorption (physiosorption and chemisorption) observed could be attributed to the fact that *A. sativum* contains many different chemical compounds which some can adsorbed chemically and others adsorbed physically. This observation may be attributed to the fact that adsorbed organic molecules can influence the behavior of electrochemical reactions involved in corrosion processes in several ways. The action of organic inhibitors depends on the type of interactions between the substance and the metallic surface. The interactions can bring about a change either in electrochemical mechanism or in the surface available for the processes (41).

Table 3. Some parameters of linear regression from Langmuir isotherms plot for aluminum corrosion in 0.1 M HCl containing extract of *A. sativum*.

System/concentration	Temperature (K)	$\Delta G$ (kJ/mol)	Slope	K	$R^2$
Extract	303	−18.64	1.00	29.41	0.99
	313	−21.05	1.03	58.82	0.99
	323	−23.75	1.04	125.00	0.99
	333	−24.86	1.03	142.86	0.99

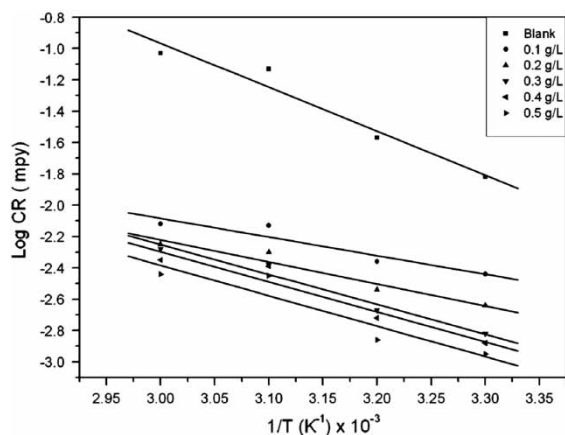
### Effect of temperature

Temperature plays an important role on metal dissolution. The corrosion rate in acid solution, for example, increases exponentially with temperature increase because the hydrogen evolution overpotential increases (42). In order to access the effect of temperature on the corrosion and corrosion inhibition process, weight loss experiments were carried out in the temperature range 303–333 K in 0.1 M HCl in the absence and presence of different concentrations (0.1–0.5 g/L) of *A. sativum* extract. It was found that after 168 h immersion period, the corrosion rate in both uninhibited and inhibited acids increases with rise in temperature (Table 1). Inhibition efficiency was also found to increase with increase in temperature at all the concentrations of the extract studied. An Arrhenius-type dependence is observed between corrosion rate and temperature often expressed as:

$$CR = Ae^{(-E_a/RT)}, \quad (9)$$

where CR is the corrosion rate,  $E_a$  is the apparent activation energy,  $R$  is the molar gas constant,  $T$  is the absolute temperature, and  $A$  is the frequency factor.

Figure 4 depicts an Arrhenius plot (logarithm of CR against the reciprocal of temperature ( $1/T$ )) for aluminum in 0.1 M HCl solution in the absence and presence of different extract concentrations.

Figure 4. Arrhenius plot for aluminum corrosion in 0.1 M HCl for blank and different concentrations of *A. sativum*.

Satisfactory straight lines of high correlation coefficients were obtained. The values of activation energy were obtained from the slopes of the linear plots and are given in Table 4. It is clear that  $E_a$  values in the presence of the different concentrations of the extract are lower than in their absence. The decrease in apparent activation energy in the presence of the extract denotes chemical adsorption while the reverse is usually attributed to physical adsorption (43). This conclusion is denoted by the increase in inhibition efficiency with increasing temperature (Table 1). Similar result has been reported by Okafor et al. (44) on the inhibition of acid corrosion of carbon steel using aqueous extract of *P. amarus* seeds and leaves. Moreover, the increase in activation energy is proportional to the inhibitor concentration, indicating that the energy barrier for the corrosion process is also increased (45).

An alternative formulation of Arrhenius equation is (46):

$$CR = \left[ \frac{RT}{Nh} \right] \exp \left[ \frac{\Delta S^\circ}{R} \right] \exp \left[ \frac{\Delta H^\circ}{RT} \right], \quad (10)$$

where  $h$  is the Planck's constant,  $N$  is the Avogadro's number,  $T$  is the absolute temperature,  $R$  is the universal gas constant,  $\Delta S^\circ$  is the entropy of activation, and  $\Delta H^\circ$  is the enthalpy of activation. Figure 5 shows a plot of  $\text{Log}(CR/T)$  as a function of  $1/T$ . Straight lines were obtained with a slope of  $(-\Delta H^\circ/R)$  and an intercept of  $(\ln R/Nh + \Delta S^\circ/R)$  from which the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated

Table 4. Calculated values of activation parameters for aluminum corrosion in 0.1 M HCl in the absence and presence different concentrations of *A. sativum* extract.

Systems/ Concentrations	$E_a$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)
Blank (0.1 M HCl)	53.8	51.3	−61.65
0.1 g/L extract	22.8	20.9	−85.97
0.2 g/L extract	27.0	24.5	−79.75
0.3 g/L extract	36.6	34.7	−87.88
0.4 g/L extract	36.8	34.5	−88.75
0.5 g/L extract	37.1	34.5	−90.47

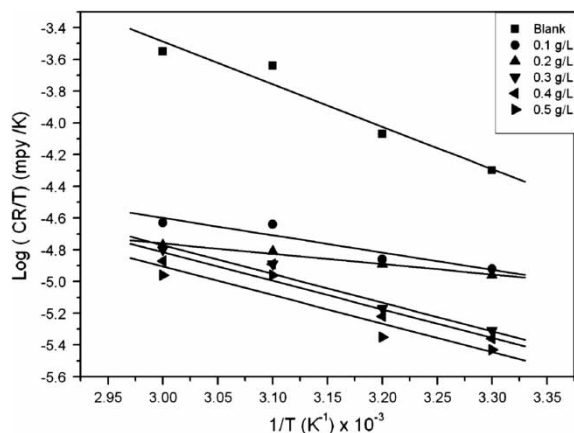


Figure 5. Transition state plot for aluminum corrosion in 0.1 M HCl for blank and different concentrations of *A. sativum*.

and listed in Table 4. The positive values of  $\Delta H^\circ$  both in the absence and presence of the extract reflect the endothermic nature of the aluminum dissolution process. It is also clear that the activation enthalpies vary in the same manner as the activation energies, supporting the proposed inhibition mechanism. Large and negative values of entropies imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. Similar observation has been reported in the literature (46).

## Experimental

### Materials

Materials used for the study were Al sheets of type AA1060 and purity 98% obtained from System Metal Industries Calabar, Nigeria. The sheet was mechanically pressed cut into coupons of dimensions  $5 \times 4 \times 0.08$  cm. Each coupon was degreased by washing with absolute ethanol, dried in acetone, and preserved in a desiccator prior to use in corrosion testing. All reagents used for the study were Analar grade and were used as received without further purification. Double distilled water was used for the preparation of all reagents.

### Preparation of extract of *Ananas sativum*

Samples of *A. sativum* were sun-dried and ground to fine powder. About 1.5 kg of the powdered sample was extracted using 80% ethanol for 72 h. The extract was concentrated initially using vacuum evaporator and finally by evaporation to dryness on a steam bath to obtain a solid extract devoid of ethanol. From the

solid extract, different concentrations (0.1–0.5 g/L) were weighed and dissolved in 0.1 M HCl solution for weight loss measurements and in 2 M HCl for hydrogen evolution measurements.

### Weight loss measurements

Weight loss measurement was carried out following the procedures reported elsewhere (25–30). The volume of test solution was kept at 100 mL. After 24 h of immersion, each coupon was retrieved from the solution, washed in solution of 70%  $\text{HNO}_3$ , dried in acetone, and weighed. The samples were subsequently returned to their respective test solutions and the procedure repeated progressively for 168 h (7 days). The weight loss was taken as the difference between the weight at a given time and the original weight of the coupons.

From weight loss measurements, inhibition efficiency (I%), and corrosion rates (CR) were calculated using Equations (11) and (12), respectively:

$$\text{Inhibition efficacy, I\%} = \frac{W_0 - W_1}{W_0} \times 100 \quad (11)$$

$$\text{Corrosion (mpy)} = \frac{534W}{\rho At}, \quad (12)$$

where  $W_0$  and  $W_1$  are the initial and final weights of the coupon, respectively.  $W = (W_0 - W_1)$  is the weight loss (mg),  $\rho$  is the density of the coupon ( $\text{g/cm}^3$ ),  $A$  is the area of the specimen ( $\text{in}^2$ ), and  $t$  is the exposure time (h).

### Hydrogen evolution method

The apparatus and procedure used for hydrogen evolution method was similar to that described in literature (15,24). The test solution was kept at 100 mL. The progress of the corrosion reaction was monitored by careful measurement of the volume of hydrogen gas evolved at fixed time intervals. From the volume of hydrogen gas evolved per minute, inhibition efficiency (I%) was calculated using Equation (13):

$$\text{I\%} = \left[ 1 - \frac{V_{\text{H}_2}^1}{V_{\text{H}_2}^0} \right] \times 100, \quad (13)$$

where  $V_{\text{H}_2}^1$  is the volume of hydrogen evolved at time  $t$  for inhibited solution and  $V_{\text{H}_2}^0$  is the volume of hydrogen evolved at time  $t$  for uninhibited solution.

## Conclusion

On the basis of this study the following conclusions can be drawn:



- (1) The crude extract of *A. sativum* acts as inhibitor for aluminum corrosion in acidic medium.
- (2) Inhibition efficiency of the extract increases with increase in concentration of the inhibitor and also with increase in temperature.
- (3) The corrosion inhibition is probably due to the adsorption of the phytochemical constituents of the extract on the metal surface and blocking its active sites by phenomenon of chemical adsorption.
- (4) The extract was found to obey Langmuir adsorption isotherm from the fit of the experimental data at all the concentrations and temperatures studied.
- (5) The values of  $E_a$  obtained in the presence of the extract were lower compared to the blank acid solution which further support the chemical adsorption proposed.
- (6) The values of  $\Delta G_{ads}^0$  obtained are low and negative, which reveals the spontaneity of the adsorption process.

## References

- (1) Khaled, K.F.; Al-Qahtani, M.M. *Mater. Chem. Phys.* **2009**, *113*, 150–158.
- (2) Amin, M.A.; Mohsen, Q.; Hazzaci, O.A. *Mater. Chem. Phys.* **2009**, *114*, 908–914.
- (3) Abdel-Rehim, S.S.; Hassan, H.H.; Amin, M.A. *Appl. Surf. Sci.* **2002**, *187*, 279–290.
- (4) Cao, G.; Liang, C. *J. Electrochem. Soc.* **2007**, *154*, C144–C151.
- (5) Aljourani, J.; Raeissi, K.; Golozar, M.A. *Corros. Sci.* **2009**, *51*, 1836–1843.
- (6) Khaled, K.F. *Mater. Chem. Phys.* **2009**, *112*, 290–300.
- (7) Jain, T.; Chowdhary, R.; Mathur, S.P. *Mater. Corros.* **2006**, *57*, 422–426.
- (8) Priya, S.L.A.; Chitra, A.A.; Rajendran, S.A.; Anuradha, K.B. *Surf. Eng.* **2005**, *21*, 229–231.
- (9) Jain, T.; Chowdhary, R.; Arora, P.; Mathur, S.P. *Bull. Electrochem.* **2005**, *21*, 23–27.
- (10) Ebenso, E.E.; Ekpe, U.J.; Ibok, U.J.; Umoren, S.A.; Jackson, E.; Oforka, N.C.; Abiola, O.K.; Martinez, S. *Trans. SAEST* **2004**, *39*, 117–123.
- (11) El-Etre, A.Y. *Corros. Sci.* **2003**, *45*, 2485–2495.
- (12) Davis, G.D.; Von Fraunhofer, J.A. *Mater. Perform.* **2003**, *42*, 56–60.
- (13) Kliskic, M.; Radosevic, J.; Gudic, S.; Katalinic, V. *J. Appl. Electrochem.* **2000**, *30*, 823–830.
- (14) Oguzie, E.E.; Onouchukwu, A.I.; Okafor, P.C.; Ebenso, E.E. *Pigm. Resin Technol.* **2006**, *35*, 63–70.
- (15) Oguzie, E.E. *Corros. Sci.* **2007**, *49*, 1527–1539.
- (16) Abiola, O.K.; Otaigbe, J.O.E.; Kio, O.J. *Corros. Sci.* **2009**, *51*, 1879–1881.
- (17) Abiola, O.K.; Otaigbe, J.O.E. *Corros. Sci.* **2009**, *51*, 2790–2793.
- (18) Abiola, O.K.; Oforka, N.C.; Ebenso, E.E.; Nwinuka, N.M. *Anti-Corros. Methods Mater.* **2007**, *54*, 219–224.
- (19) El-Hosary, A.A.; Saleh, R.M.; Shams El Din, A.M. *Corros. Sci.* **1972**, *12*, 879–904.
- (20) Noor, E.A. *J. Appl. Electrochem. Sci.* **2009**, *39*, 1465–1475.
- (21) Abdel-Gaber, A.M.; Khamis, E.; Abo-ElDahab, H.; Abdeel, S. *Mater. Chem. Phys.* **2008**, *109*, 297–305.
- (22) Obot, I.B.; Obi-Egbedi, N.O. *Portug. Electrochim. Acta* **2009**, *27*, 517–524.
- (23) Saleh, R.M.; Ismail, A.A.; El-Hosary, A.A. *Corros. Sci.* **1983**, *23*, 1239–1241.
- (24) Umoren, S.A.; Obot, I.B.; Ebenso, E.E.; Okafor, P.C.; Ogboode, O.; Oguzie, E.E. *Anti-Corros. Methods Mater.* **2006**, *53*, 277–282.
- (25) Umoren, S.A. *Cellulose* **2008**, *15*, 751–761.
- (26) Umoren, S.A.; Obot, I.B.; Obi-Egbedi, N.O. *J. Mater. Sci.* **2009**, *44*, 274–279.
- (27) Umoren, S.A.; Obot, I.B.; Ebenso, E.E.; Obi-Egbedi, N.O. *Desalination* **2009**, *247*, 561–572.
- (28) Umoren, S.A.; Obot, I.B.; Akpabio, L.E.; Etuk, S.E. *Pigm. Resin Technol.* **2008**, *37*, 98–105.
- (29) Umoren, S.A.; Obot, I.B.; Ebenso, E.E.; Okafor, P.C. *Portug. Electrochim. Acta* **2008**, *26*, 267–282.
- (30) Umoren, S.A.; Obot, I.B.; Ebenso, E.E.; Obi-Egbedi, N.O. *Portug. Electrochim. Acta* **2008**, *26*, 199–209.
- (31) Nguyen, T.H.; Foley, R.T. *J. Electrochem. Soc.* **1982**, *129*, 27–32.
- (32) Bhajiwala, H.M.; Vashi, R.T. *Bull. Electrochem.* **2001**, *17*, 441–448.
- (33) Mousa, M.N.; Fouda, A.S.; Taha, F.I.; Elnenna, A. *Bull. Korean Chem. Soc.* **1988**, *9*, 191–195.
- (34) Abdallah, M. *Portug. Electrochim. Acta* **2004**, *22*, 161–175.
- (35) Aytac, A.; Oxmen, U.; Kabasakaloglu, M. *Mater. Chem. Phys.* **2005**, *89*, 176–181.
- (36) Damaskin, B.B.; Petrii, O.A.; Batrakov, V.V. *Adsorption of Organic Compound on Electrodes*; Plenum: New York, 1971.
- (37) Bockris, J.O.M.; Khan, S.U.M.; *Surface Electrochemistry: A Molecular Level Approach*; Plenum: New York, 1993.
- (38) Karakus, M.; Sahin, M.; Bilgic, S. *Mater. Chem. Phys.* **2005**, *92*, 565–571.
- (39) Refaey, S.A.M.; Taha, F.; Abd-El-Malek, M. *Appl. Surf. Sci.* **2004**, *236*, 175–181.
- (40) Noor, E.A. *Int. J. Electrochem. Sci.* **2007**, *3*, 996–1017.
- (41) Aramaki, K.; Hackermann, N. *J. Electrochem. Soc.* **1969**, *116*, 568–571.
- (42) de Souza, F.S.; Spinelli, A. *Corros. Sci.* **2009**, *51*, 642–649.
- (43) Awad, M.I. *J. Appl. Electrochem.* **2006**, *36*, 1163–1168.
- (44) Okafor, P.C.; Ikpi, M.E.; Uwah, I.E.; Ebenso, E.E.; Ekpe, U.J.; Umoren, S.A. *Corros. Sci.* **2008**, *50*, 2310.
- (45) Popova, A.; Sokolova, E.; Raicheva, S.; Christov, M. *Corros. Sci.* **2003**, *45*, 33–58.
- (46) Fouda, A.S.; Al-Sarawy, A.A.; Ahmed, F.S.; El-Abbasy, H.M. *Corros. Sci.* **2009**, *51*, 485–492.