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Thermodynamics, Kinetics and Adsorption Studies of *Andrographis Paniculata* as a Green and Nontoxic Corrosion Inhibitor of Commercial Structural Aluminium in 0.5 M HCl and H_2SO_4 Solutions

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Abstract

The corrosion inhibition performance of ethanol extract of *Andrographis paniculata* (EEAP) on the corrosion of Aluminum in 0.5 M HCl and H_2SO_4 acid solutions at 303K and elevated temperatures of 313, 323 and 333K was investigated and compared. The experimental work was performed by the use of gravimetric and gasometric techniques. The results indicated that the extract inhibit the corrosion of aluminum perfectly in both media. However, the EEAP exhibits highest inhibition efficiency in HCl (95.4%) than in H_2SO_4 (85.8%) at 5.0 g/L. Generally inhibition efficiency was found to increase with increased concentration of inhibitor in both acid media but decreased with rise in temperature. Inhibition mechanism was deduced from the temperature dependence of the inhibition efficiency as well as from activation parameters that govern the process. Adsorption of extract on the aluminum coupon in both acid media was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption was proposed from the obtained thermodynamic parameters as equilibrium constant (K_{ad}) showed a decrease with increased temperature, free energy of adsorption ($-\Delta G_{ads}$) values were more negative than 20 $kJmol^{-1}$, standard enthalpy of activation (ΔH) values were low (i.e < 100 $kJmol^{-1}$). Kinetic data revealed a 1st order reaction as values were fitted the integrated rate equation plot and negative slope obtained.

Keywords: Aluminum, Thermodynamics, Inhibition Efficiency, Corrosion.

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1. Introduction

Metallic materials are still the most widely used group of materials particularly in both mechanical engineering and the transportation industry. In addition, metals are commonly used in electronics and increasingly also in the construction industry [1]. Aluminum is the second most widely specified metal in buildings after steel, and is used in all construction sectors, from commercial buildings to domestic dwellings [1-2]. It is fitting for residential and commercial buildings as it is resistant to mold, lightweight, provide strong support and gives desire options. The main market sectors for aluminum are windows, , roofing, cladding, curtain walling and structural glazing, prefabricated buildings, architectural hardware, shorp fittings and partitions [2,3]. Environmentally friendly inhibitors have attracted many researchers. Corrosion damage can be prevented by using various methods such as upgrading materials, blending of production fluids, process control and chemical inhibition [2]. The known effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products [3]. Natural products are nontoxic, biodegradable and readily available. They have been used widely as inhibitors. So many natural products have been used as inhibitors in the corrosion of metals especially mild steel [1,4]. Aluminum, carbon steel etc. Corrosion inhibition investigation of natural inhibitors is particularly interesting because they are inexpensive, ecologically friendly, and possess no threat to the environment [5-7]. The present work is undertaken to evaluate the inhibition efficiency (IE%) of an aqueous extract of *Andrographis paniculata* (King bitter) in controlling the corrosion of Aluminum in hydrochloric (HCl) and sulphuric (H_2SO_4) acids media and to propose a suitable mechanism for corrosion inhibition by understanding the thermodynamics, kinetics and adsorption parameters of the inhibitors.

2. Materials and methods

2.1 Material Preparation

The sheet of aluminium used for this experiment has the following chemical composition: Al (99.95 %), Cu (0.01 %), Mg (0.02 %), Si (0.02 %), Mn (0.002 %) and Zn (0.005 %) were obtained commercially from System Metals Nig. Ltd. Calabar, Nigeria. The sheets were mechanically press-cut into 4.00 x 0.08 x 5.00cm coupons. These were polished with different grades of emery paper (200, 800 and 1200), degreased in absolute ethanol, dried in acetone and stored in a moisture free desiccator prior to use after air drying. The aggressive acidic solutions of 0.5 M HCl and H_2SO_4 were prepared by dilution of analytical grade HCl and H_2SO_4 with distilled water. All experiments were carried out in unstirred solutions and all weighing was done with digital analytical balance.

2.2 Preparation of plant extract (A. *paniculata*)

The required leaves – *A. paniculata* were collected from the local bush in Nigeria. These leaves were dried in a laboratory Oven at a minimal temperature to avoid loss of major organic components of the plant and ground into powder form. The powdered sample was extracted continually with absolute ethanol in a Soxhlet Extractor for 12 hours. The extract obtained was later heated on a water bath at a temperature of 60°C until most of the ethanol evaporated. 5g of the ethanol extract of the plant was diluted with appropriate volume of the HCL and H_2SO_4 acid solutions then kept for approximately 24 hours, filtered and stored. From the stock solution (5 g/L), inhibition test solutions were prepared to obtain 0.5 g/L, 1.0 g/L, 2.0 g/L, 3.5 g/L and 5.0 g/L for weight loss and hydrogen evolution measurements respectively.

2.3 Gravimetric measurements

Weighed test pieces were fully immersed, separately for 10 hours in each of the beakers containing the 0.5 M HCl and solution extract for the five sets of the experiment described above, and acid medium without the extract addition. The same process as above was done for the beakers containing 0.5 M H_2SO_4 acid. Each of the test specimens was taken out every one hours, washed with distilled water, rinsed with ethanol, dried with acetone and re-weighed. Plots of weight loss vs exposure time were made were corrosion rates were obtained and subsequently inhibition efficiency obtained from the equation (1) and (2):

$$\Theta = 1 - \frac{W1}{W2} \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 1$$

$$IE\% = \theta \, x \, 100 \ \ldots \quad \ldots \quad \ldots \quad \ldots \qquad 2$$

2.4 Gasometric measurements

In monitoring corrosion studies using this technique, 100 mL of the corrodent (0.5 M HCl) was introduced into the two-necked flask and the initial volume of the air in the burette was noted. Thereafter, an aluminium coupon of dimension 1.20 cm x 0.08 cm x 4.00 cm already weighed was dropped into the corrodent and the flask was quickly closed. The volume of the hydrogen gas evolved from the corrosion reaction was monitored by volume changes in the level of paraffin oil in the graduated burette every minute for 30 minutes. In another experiment, a set of fresh coupons were immersed in the flask containing the corrodent at different concentrations each of *A. paniculata* leaves extract (0.5 g/L, 1.0 g/L, 2.0 g/L, 3.5 g/L and 5.0 g/L). The study was conducted at 303K, 313 K, 323 K and 333 K using a Thermostat water bath. This experiment above was repeated for the 0.5 M H_2SO_4 stock solution. Each experiment was repeated twice to ensure reproducibility, and the average values were recorded.

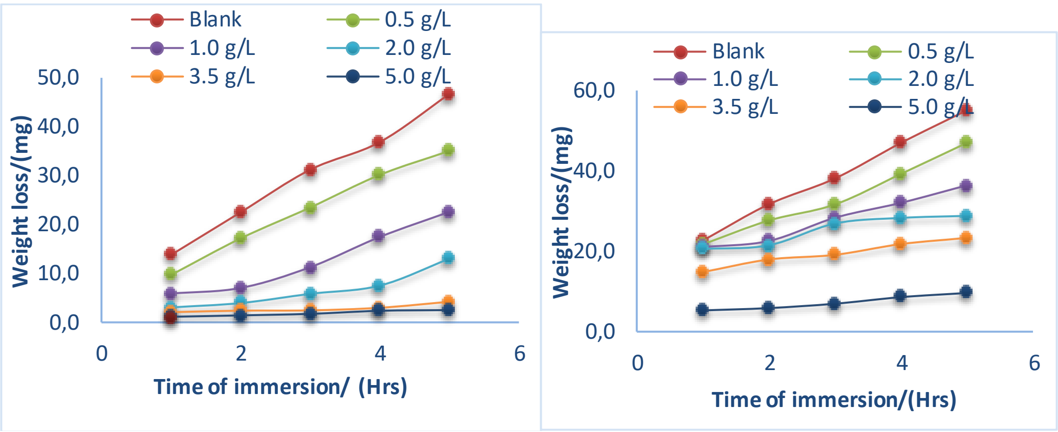
3.0 Results and Discussion

3.1 Analysis of results from gravimetric measurements

The results obtained for the variation of weight loss with exposure time for the aluminium test specimen immersed in the two test media – 0.5 M HCl and 0.5 M H_2SO_4 are presented in Fig. 1. The recorded values obtained for the tests performed without any extract addition are also presented in each of the figures. An increase in weight loss of the test specimens with exposure time was recorded for the five concentrations of the plant extract addition for both tests (Figure 1) [5-7]. More loss of weight for the test specimens was, however, observed in the test in which there was no *A. paniculata* extract added [4-6]. The aluminium reacted with HCl to displace hydrogen and gave aluminium chloride ($AlCl_3$). The reaction is given is given as:

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$$

The solubility of $AlCl_3$ decreases with increasing time of exposure, hence the gradual setting in of passivation as compared with the Al_2O_3 formed by H_2SO_4 [8-9].



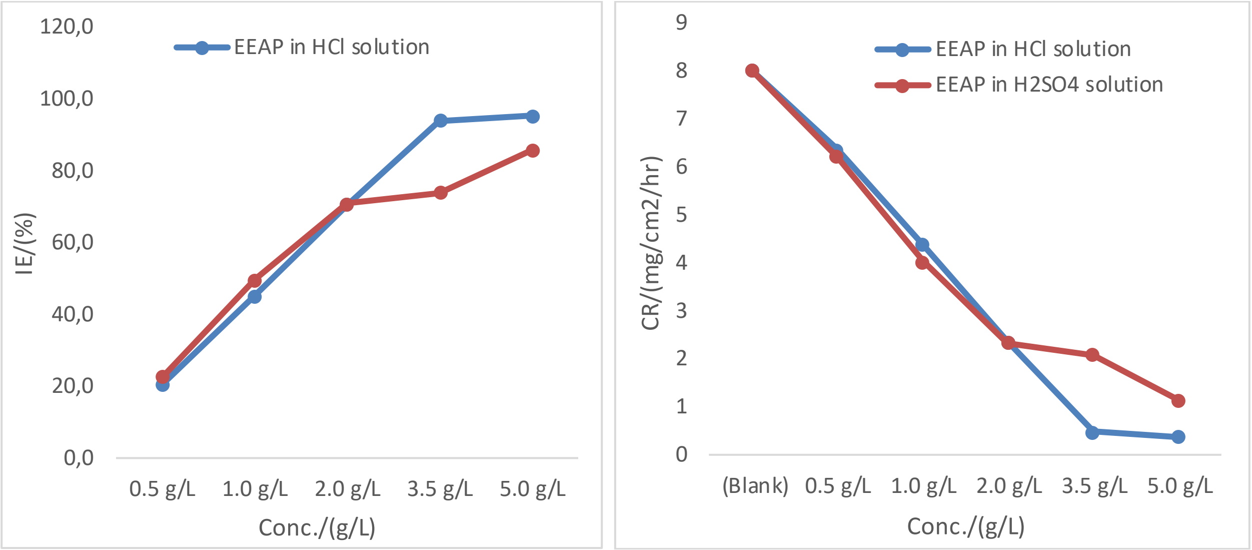
(a) (b)

Fig. 1: Variation of weight loss with immersion time for Aluminium in (a) 0.5 M HCl and (b) 0.5 M H_2SO_4 solutions in the presence and absence of *A. paniculata*

Table 1: Calculated values of corrosion rates, surface coverage and inhibition efficiency for Aluminium coupons in 0.5 M HCl and H_2SO_4 in the absence (blank) and presence of EEAP.

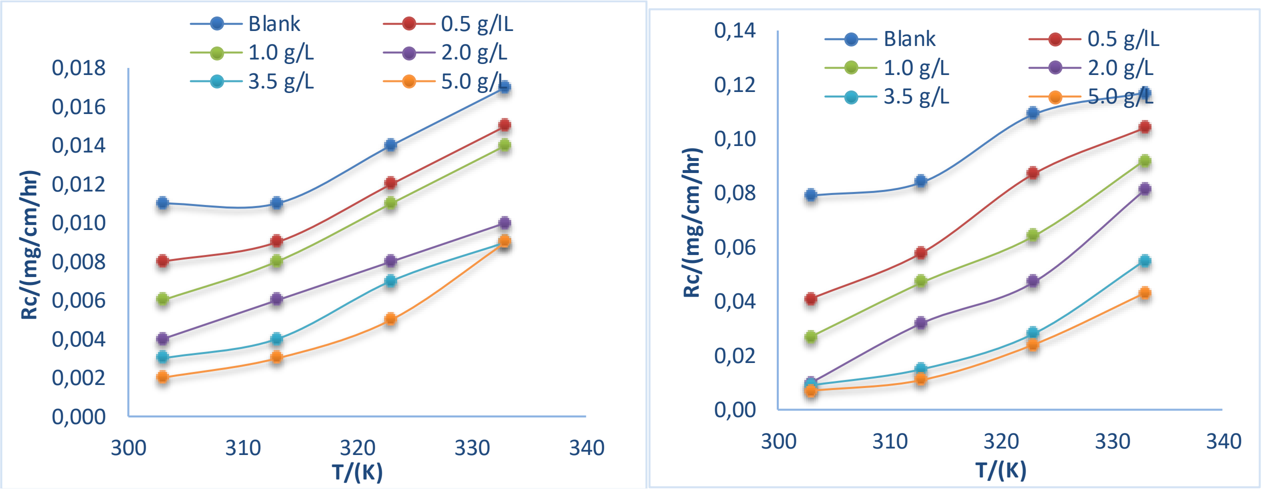
	EEAP in HCl solution			EEAP in H_2SO_4 solution		
System	CR (mg/cm²/hr)	ϴ	IE %	CR (mg/cm²/hr)	ϴ	IE %
(Blank)	8.016	-	-	8.014	-	-
0.5 g/L	6.37	0.21	20.5	6.211	0.22	22.5
1.0 g/L	4.383	0.45	45.3	4.022	0.50	49.8
2.0 g/L	2.348	0.71	70.7	2.326	0.71	71.0
3.5 g/L	0.485	0.94	93.9	2.087	0.74	74.0
5.0 g/L	0.368	0.95	95.4	1.141	0.86	85.8

However, weight loss for aluminium was also found to decrease with increase in the concentration of *A. paniculata* inhibitor indicating that the inhibitor retarded the rate of corrosion of mild steel in solutions of HCl and H_2SO_4 [4, 8-9] as indicated in Table 1 and Fig. 3. Surface coverage (θ) and inhibition efficiency (%IE) increased with increase in EEAP concentration, indicating that the corrosion of the metal has been inhibited and a larger fraction of the surface is protected against acidic attack at higher inhibitor concentrations, Fig. 3 [10-13].



(a) (b)

Fig. 3: Variation of IE (%) with Conc. (g/L) for Aluminium in (a) 0.5 M HCl and (b) 0.5 M H_2SO_4 solutions in the presence and absence of *A. paniculata*



(a) (b)

Fig. 4: Variation of R_c with temperature (K) for Aluminium in the presence and absence of extracts of *A. paniculata* in (a) 5.0 M HCl and (b) H_2SO_4 solution.

3.2 Analysis of results from gasometric measurements

The following mechanism can be proposed for hydrogen evolution reaction on electrodes in acidic media [3- 5]:

i. A primary discharge step (Volmer reaction):

$$M + H_3O^+ + e \longleftrightarrow MH_{ad} + H_2O$$

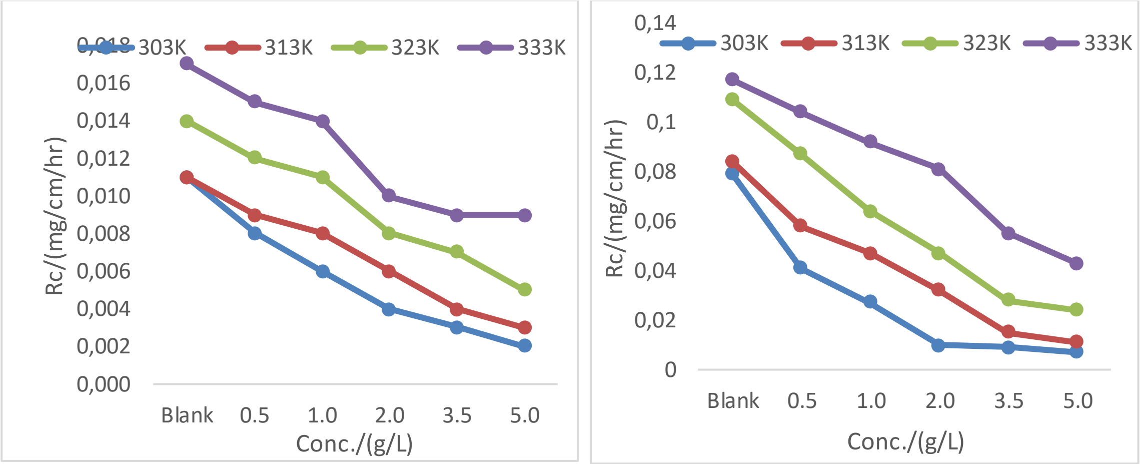
ii. An electrochemical-desorption step (Heyrowsky reaction)

$$MH_{ad} + H_3O^+ + e \longrightarrow M + H_2 + H_2O$$

iii. a recombination step (Tafel reaction):

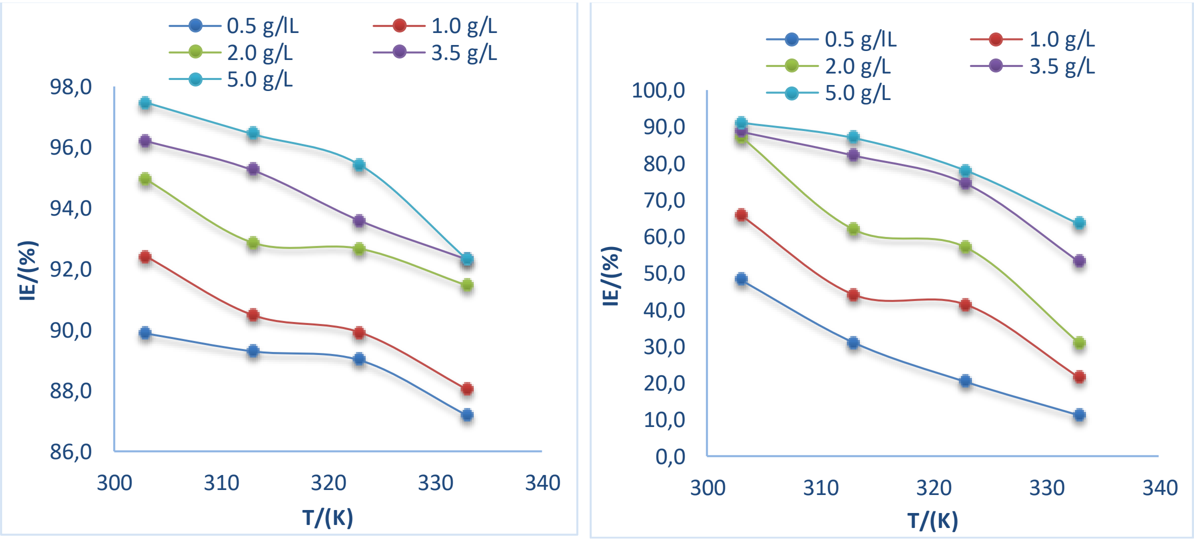
$$MH_{ad} + MH_{ad} \longrightarrow 2M + H_2$$

For hydrogen evolution reaction, the cathodic reaction may have three steps: first, water molecule or hydronium ion is discharged on electrode surface to produce hydrogen atom in acidic solution and adsorbed hydrogen atom, MH_{ad}, is generated (Volmer reaction). Second, one electron is transferred to a hydronium ion and the hydrogen evolution reaction occurs on metal surface (Heyrowsky reaction) or a pure chemical reaction takes place subsequently (Tafel reaction) [2, 5]. The results obtained however showed that the corrosion rate decreased with increase in EEAP concentrations, but increase with increase in temperature for both HCl and H_2SO_4 solutions (Fig. 4-7). From the corrosion rates, the inhibition efficiency was determined using equation 2.



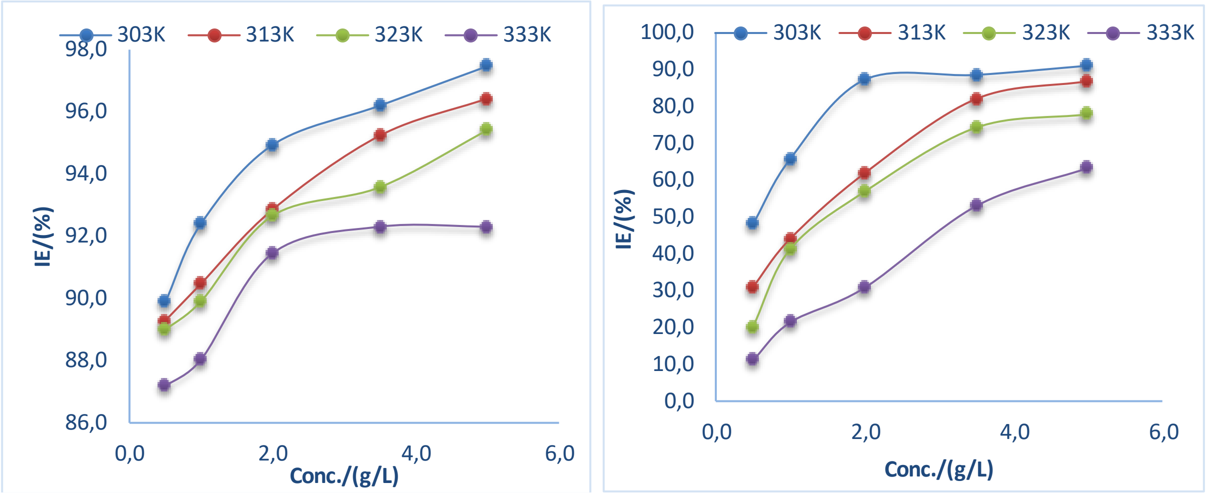
(a) (b)

Fig. 5: Variation of R_c ($mg/cm^2/hrs$) with Conc (g/L) of Aluminium in the presence and absence of *A. paniculata* inhibitor in (a) 0.5 M HCl and (b) H_2SO_4 solution.



(a) (b)

Fig. 6: Variation of IE (%) with temperature (K) of Aluminium in the presence and absence of *A. paniculata* inhibitor in (a) 0.5 M HCl and (b) H_2SO_4 solution.



(a) (b)

Fig. 7: Variation of IE (%) with Conc. (g/L) for Aluminium in the presence and absence of *A. paniculata* inhibitor in (a) 0.5 M HCl and (b) H_2SO_4 solution.

It is observed that inhibition efficiency increases with increase in extract concentration as well as decrease with increase in temperature for EEAP in both acid solutions (Fig. 6-7). This suggested that, fractions of *A. paniculata* are adsorbed on the metal surface there by protecting metal from the action of corrodent and the latter suggest a desorption phenomenon framework following weak forces of attraction due to high temperature agitation effects [10, 13, 14-16]. The trend in temperature suggests physical adsorption [7, 8, 17].

3.3 Thermodynamic/Kinetic investigation

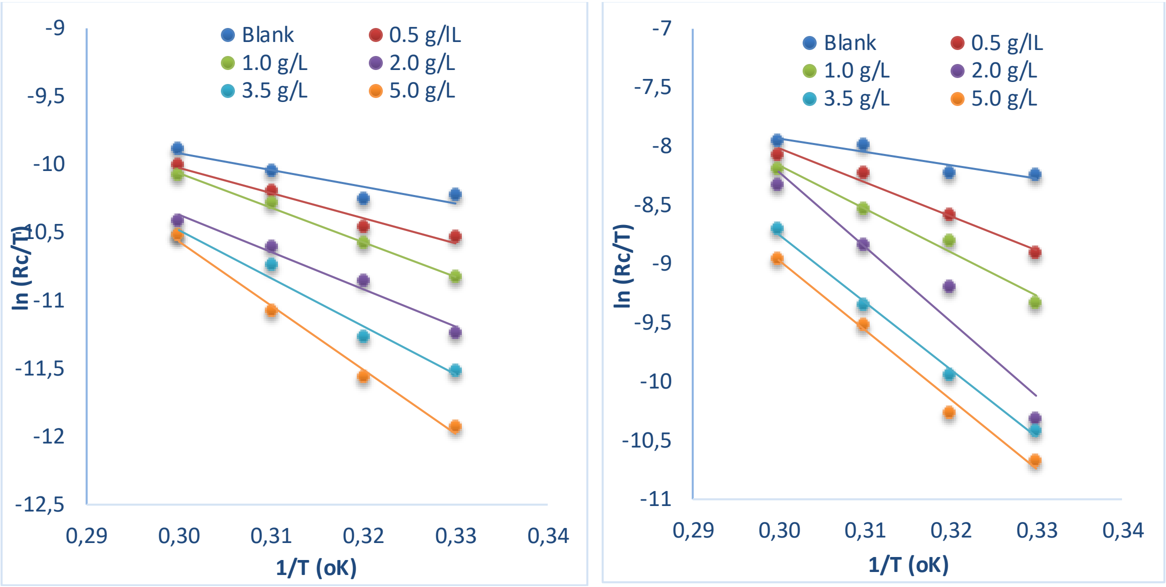
In order to determine the thermodynamic properties of the *A. paniculata*, Equation 3 being the Erying transition state equation was adopted [11, 15, 18]. A plot of log CR/T against 1/T was made to determine both enthalpy and entropy of adsorption (Fig. 8 a – b). The positive values of ΔH° indicated that the dissolution of the metal is an endothermic reaction (Table 2) [9, 15, 19-22] which suggested that aluminum dissolution required less energy in 0.5 M HCl than H_2SO_4 in the presence of inhibitor to effect bond breaking in the corrosion reaction and foster surface binding of the inhibitor [5-6, 12-14]. The change in entropy (ΔS°) was found to be greater than zero (Table 2), indicating that the reaction is irreversible [5, 10, 11]. It is clear that, the complete desorption of the inhibitor is not possible in both acid media. The shift towards negative values of entropy (ΔS°) imply that the activated complex in the rate determining step represents association rather than dissociation, meaning that disordering decreases on going from reactants to the activated complex [16, 22, - 23]:

$$\log\frac{CR}{T} = log\ \frac{R}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}\ \ldots \qquad (3)$$

The apparent activation energy (Ea) was determined from the Arrhenius plot (Fig. 9) using equation (4) [19].

$$\log\frac{P2}{P1}=\frac{Ea}{2.303R}\left(\frac{1}{T1}-\frac{1}{T2}\right) \qquad (4)$$

where P2 and P1are the corrosion rates at temperature T1 and T2 respectively, and R the molar gas constant [13, 17, 21].



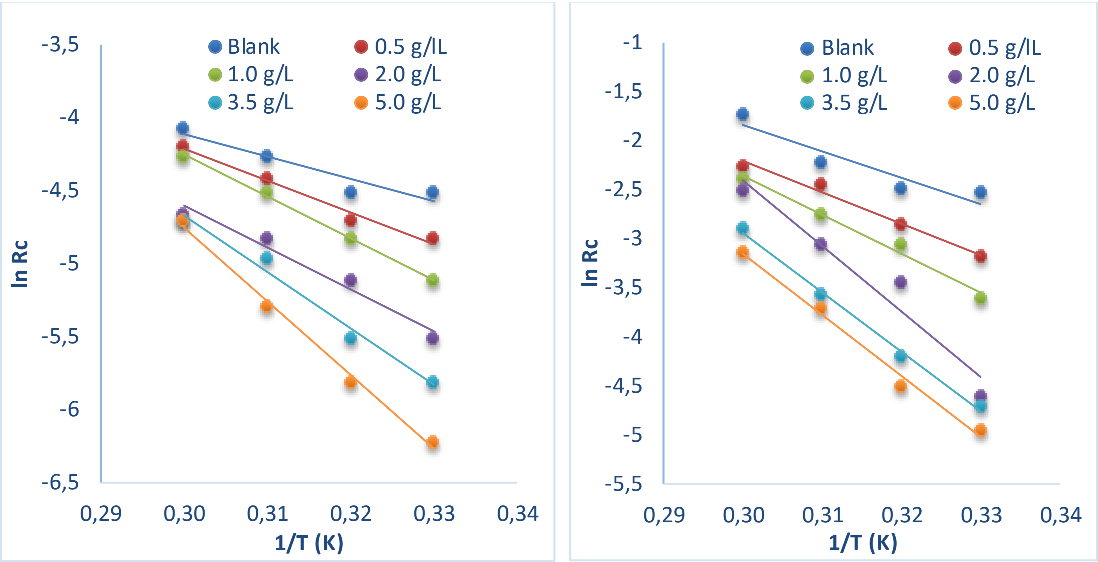
(a) (b)

Fig. 8: Eyring transition state plots for Aluminium in (a) 0.5 M HCl and (b) 0.5 M H_2SO_4 solutions in the absence and presence of EEAP inhibitor.

Table 2: Values of Activation energy/thermodynamic parameters for aluminum in 0.5 M HCl and H_2SO_4 in the absence and presence of the EEAP inhibitor

	Inhibitor in HCl solution			Inhibitor in H_2SO_4 solution		
System	Ea kJ/mol	ΔH^*_{ads} kJ/mol	ΔS^*_{ads} kJ/mol	Ea kJ/mol	ΔH^*_{ads} kJ/mol	ΔS^*_{ads} kJ/mol
Blank	12.47	10.2	-21.3	22.37	9.4	-19.6
0.5 g/L	18.13	21.1	-44	26.61	24	-50.1
1.0 g/L	23.86	22.8	-47.5	33.01	52.8	-99.2
2.0 g/L	23.86	22.8	-47.5	55.54	52.8	-102.3
3.5 g/L	32.09	29.4	-61.1	73.68	47.6	-110.0
5.0 g/L	41.90	39.2	-81.6	84.51	49.1	-110.0

Increased activation energy (Ea) in inhibited solutions compared to blank as seen in Table 2 suggested that the inhibitor is physically adsorbed on the corroding metal surface [4, 11, 20, 22]. It is seen from Table 2 that Ea values were higher in the presence of *A. paniculata* inhibitor in both 0.5 M HCl and H_2SO_4 acid solutions compared to that in their absence which explained a possible decrease in corrosion rates. This is in agreement with the fact that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [3, 9, 15]. The Ea values support the earlier proposed physisorption mechanism.



(a) (b)

Fig. 9: Arrhenius plots for Aluminium in (a) 0.5 M HCl and (b) 0.5 M H_2SO_4 solutions in the absence and presence of ethanol extract of *A. paniculata*

The kinetics of the dissolution of aluminium by hydrochloric and sulphuric acids solutions without and with different concentrations (0.5 g/L, 1.0 g/L, 2.0 g/L, 3.5 g/L and 5.0 g/L) of the *A. paniculata* inhibitor was studied by fitting the corrosion data into different rate laws [23 - 25]. According to equation 5, when $\ln(W_o/W_i)$ was plotted versus time, a linear variation with a negative slope was obtained indicating first- order reaction kinetics in both HCl and H_2SO_4 solutions in the present of the different inhibitor concentrations [24 – 25]:

$$ln\frac{Wo}{Wi} = -kt \qquad \dots\dots \qquad \dots \qquad 5$$

where k is the rate constant. This result in Table 3 suggests an inhibition of the dissolution process without affecting the reaction order as the rate constant values were decreasing with increased inhibitor concentration in both acidic solutions [23, 25-27]. This could also be confirmed from the half-life values approaching 45,000 hrs and 21,000 hrs at a maximum concentration of 5.0 g/L in HCl and H_2SO_4 solutions respectively. In the same vein, equation 6 and 7for 1st and 2nd order integrated rate laws were adopted to ascertain graphically what order is the inhibitor reaction.

$$\ln[A] = -kt + \ln[A]_o \dots \qquad \dots \qquad \dots \qquad 6$$

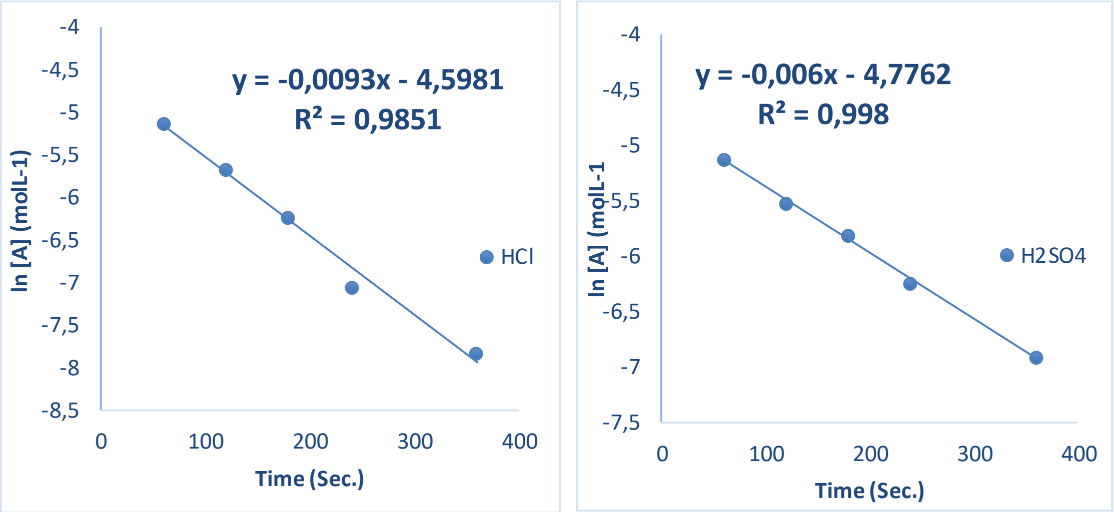
$$\frac{1}{[A]_t} = \frac{1}{[A]_o} + kt \dots \qquad \dots \qquad \dots \qquad \dots \qquad 7$$

where [A] is the concentration of reactant, k is the rate constant, t is the time, $[A]_o$ is the initial concentration and $[A]_t$ is the specific concentration at time t.

Table 3: Kinetic data for EEAP in 0.5 M HCl and H_2SO_4 acid solutions

	Extract in HCl solution		Extract in H_2SO_4 solution	
System	Rate con K (Hrs)	Half life $t_{1/2}$ (Hrs)	Rate con K (Hrs)	Half life $t_{1/2}$ (Hrs)
0.5 g/L	0.151	4,589.4	0.180	385.0
1.0 g/L	0.098	7,071.4	0.126	550.0
2.0 g/L	0.097	7,144.3	0.096	7,218.8
3.5 g/L	0.086	8,058.1	0.080	8,662.5
5.0 g/L	0.016	43,312.5	0.034	20,382.4

It was observed that inhibitor reaction was a 1st order reaction as data fit very well to the plot and negative slope was obtained (Fig. 10a - b) [25, 26 – 27]. This confirmed the linear dependency of the reaction on concentration of only one reactant [26-27]. The data did not fit into the second order rate law even though positive slope was obtained as seen in Fig. 11a – b.



(a) (b)

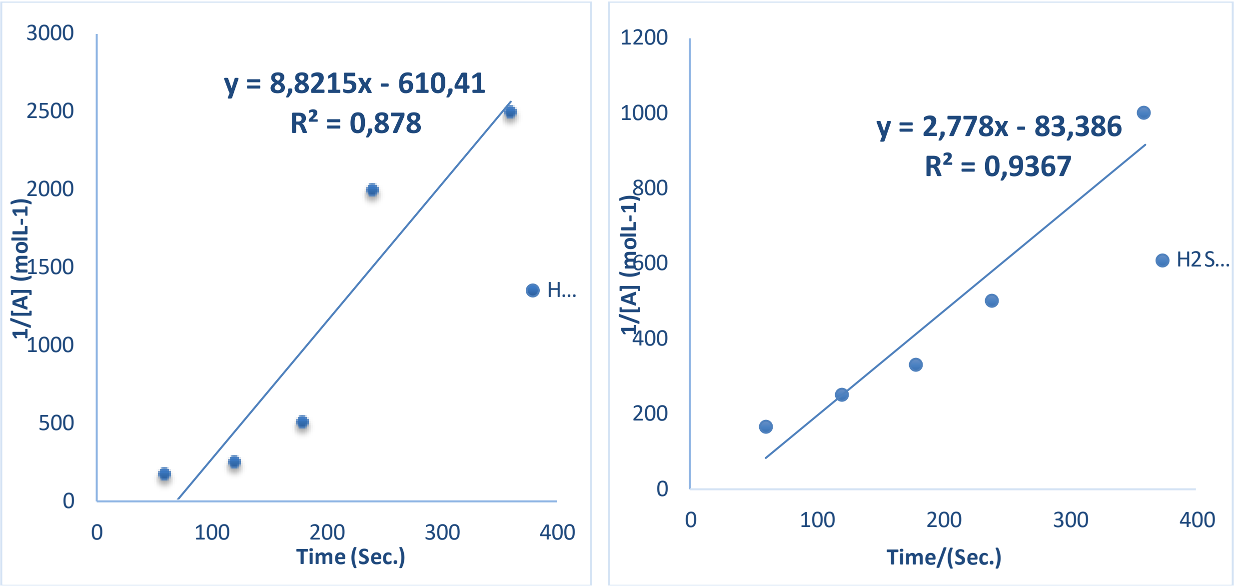
Fig. 10 Kinetic plots for the 1st order integrated rate law for Aluminium in (a) 0.5 M HCl and (b) 0.5 M H_2SO_4 solutions in the absence and presence of ethanol extract of *A. paniculata*

3.4 Adsorption consideration

Values of surface coverage (ϴ) were tested graphically for fit to different isotherms using equation 8. [19, 21, 28 – 30] :

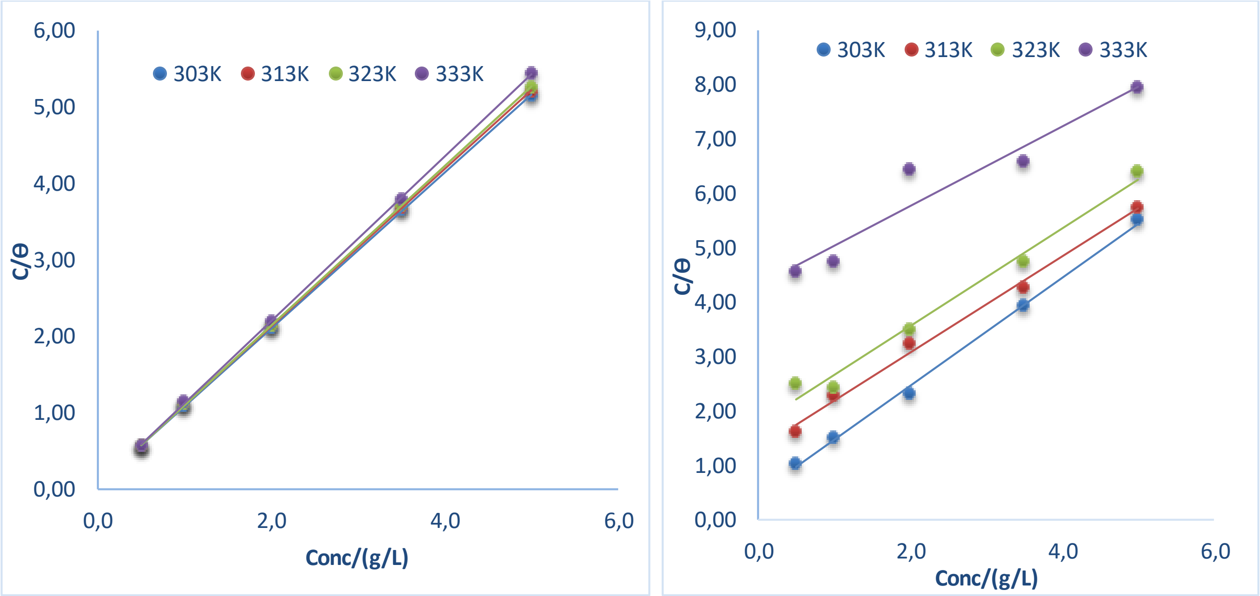
$$\frac{C}{\theta} = \frac{1}{Kads} + C \qquad (8)$$

where ϴ is the degree of surface coverage, k the equilibrium constant of the adsorption - desorption process and C the concentration of the inhibitor in the electrolyte [26, 16, 31]. As shown in Fig. 12, a straight line was obtained for the *A. paniculata* inhibitor in both HCl and H_2SO_4 acid solutions when C/ϴ was plotted against C.



(b) (b)

Fig. 11 Kinetic plots for the 2nd order integrated rate law for Aluminium in (a) 0.5 M HCl and (b) 0.5 M H_2SO_4 solutions in the absence and presence of ethanol extract of *A. paniculata*



(a) (b)

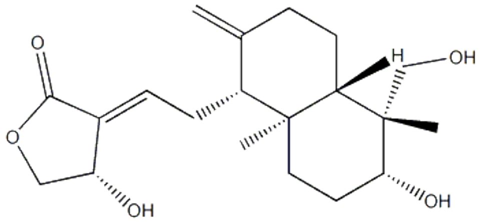
Fig. 12: Langmuir adsorption isotherm for mild steel samples in (a) 0.5 M HCl and (b) 0.5 M H_2SO_4 solutions containing EEAP

The linear correlation coefficient values of the fitted data were generally good but with a better fitting for the inhibitor in HCl (0.999) as seen in Table 4. This indicates that the adsorption behaviour was consistent with Langmuir adsorption (a monolayer chemical adsorption) [22 – 24, 31-33]. Values of equilibrium constant of the inhibitor were seen to be larger in HCl as well as decreasing with temperature compared to smaller and increasing values for inhibitor in H_2SO_4 indicating that the inhibitor was much better in HCl than H_2SO_4. This has also been confirmed from the unity values of the slope for HCl compared to H_2SO_4.

Table 4: Adsorption parameters for Aluminium in 0.5 M HCl and H_2SO_4 solutions containing EEAP using hydrogen evolution technique

	EEAP in HCl solution			EEAP in H_2SO_4 solution		
Temp. (K)	Eq. Cons K (g/L)	R^2	Slope	Eq. Cons K (g/L)	R^2	Slope
303	20.492	1.000	1.0764	0.2323	0.9211	0.7310
313	17.667	0.999	1.0304	0.5671	0.9831	0.8977
323	14.472	0.999	1.0431	0.7674	0.9930	0.8845
333	15.504	0.999	1.0198	2.1022	0.9972	0.9906

Active compounds extracted with ethanol or methanol from the whole plant, leaf and stem include over 20 diterpenoids and over ten flavonoids have been reported from *A. paniculate* among andrographolide ($C_{20}H_{30}O_5$) is the major diterpenoid [34-37] of general structure:



Andrographolide activity against several deceases as bacteria and virus infections, cancers… are widely documented [38-42].

As the natural extract contains infinite components at various contents [34-37], the retardation of corrosion reaction is due to the various active molecules of the natural extract; we may introduce that inhibitory effect is conducted by the intermolecular synergistic effect of several molecules [43-46].

4. Conclusion

The findings revealed that:

1. *Andographis paniculata* acted as a good eco-friendly inhibitor in both hydrochloric and Hydrogen Tetraoxosulphate (VI) acid solutions with surface coverage area of metal at 0.95 and 0.86 cm^2 for HCl and H_2SO_4 respectively.
2. *Andographis paniculata* showed better inhibition qualities from the measured thermodynamics, kinetics and adsorption parameters in HCl solutions compared to H_2SO_4 with inhibition efficiency difference of 9.6 %.
3. Thermodynamics results present *A. paniculata* as an inhibitor that is spontaneous in reaction, associative at its activation complex, endothermic (enhancing bond breaking in the corrosion reaction process), physically adsorbed and stabled on the metal surface.
4. Kinetic data revealed an inhibitor with a large half-life, and an inhibitor that is 1st order hence,

depending linearly on the concentration of only one reactant to effect inhibition. A process that is associated with a good inhibitor.

5. Adsorption investigation showed that *A. paniculata* as inhibitor was physically adsorbed, obeyed the monolayer chemical adsorption mechanism (Langmuir isotherm).

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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