Fountain Journal of Natural and Applied Sciences: 2013; 2(2): 10 - 21

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DOI: 10.53704/fujnas.v2i2.26

A publication of College of Natural and Applied Sciences, Fountain University, Osogbo, Nigeria
Journal homepage: www.fountainjournals.com
ISSN: 2354-337X (Online), 2350-1863 (Print)

Corrosion Inhibition Effects and Adsorption Characteristics of Ethanol Extract of King Bitters Root (*Andrographis paniculata*) on Mild Steel in Hydrochloric and Tetraoxosulphate (VI) Acid Media

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Abstract

The corrosion inhibition performance of ethanol extract of Andrographis paniculata (King Bitter) root (EEAPR) on the corrosion of Mild Steel (MS) in 1.0 M HCl and H_2SO_4 acid solutions at 303 K and elevated temperatures of 313, 323 and 333 K was investigated and compared. The experimental work was performed by the use of weight loss and hydrogen evolution techniques. The results indicate that the extract inhibit the corrosion of mild steel in both acid media. However, the EEAPR exhibits higher maximum inhibition efficiency of 98.9 % in HCl than in H_2SO_4 (95.0 %) at 5.0 g/L. Inhibition efficiency was found to increase with increasing concentration of extract 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 MS sample in both acid media was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters.

Key words: *Weight loss, Thermodynamics, Inhibition efficiency, Surface coverage, Hydrogen evolution.*

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 (Uwah *et al.*, 2013). Environmental 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 (Shastri, 1998). The known effects of most synthetic corrosion inhibitors e.g. reversible (temporary) or irreversible (permanent) damage to organ system, namely, kidneys or liver, or disturbance of a biochemical process or disturbance of an enzyme system at some site in the body are the motivation for the use of some natural products (Wranglan, 1985). Natural products are nontoxic, biodegradable and readily available. So many natural products have been used as inhibitors in the corrosion of metals especially mild steel,

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aluminum, carbon steel, etc. (Uwah *et al.,* and Rajam *et al.*, 2013). Corrosion inhibition investigation of natural inhibitors is particularly interesting because they are inexpensive, ecologically friendly, and possess no threat to the environment (Devi and Rajendran, 2011; Okafor *et al.,* 2007 and Oguze, 2005). This study evaluates the inhibition efficiency (IE %) of an aqueous extract of *Andrographis paniculata* (King bitter) root in controlling the corrosion of Corrosion inhibition investigation of natural inhibitors is particularly interesting because they are inexpensive, ecologically friendly, and possess no threat to the environment (Devi and Rajendran, 2011; Okafor *et al.,* 2007 and Oguze, 2005). This study evaluates the inhibition efficiency (IE %) of an aqueous extract of *Andrographis paniculata* (King bitter) root in controlling the corrosion of aluminium in hydrochloric (HCl) and Tetraoxosulphate (VI) acid (H_2SO_4) acids media and to propose a suitable mechanism for corrosion inhibition.

Experimental

Material Preparation

The sheet of Mild steel used for this experiment has the following chemical composition: Fe (98.34%) C (0.19%), Si (0.26%), Na (0.64%), S (0.05%), P (0.06%), Ni (0.09%), Cr (0.08%), Mo (0.02%), and Cu (0.27%). respectively. The sheets were mechanically press-cut into 4.00 x 0.08 x 5.00cm samples. These were polished with different grades of emery paper, degreased in absolute ethanol, dried in acetone and stored in a moisture free desiccator prior to use (Okafor *et al.*, 2007; Uwah *et al.*, 2013 and Ebenso *et al.*, 2008). The aggressive acidic solution of 1.0 M HCl and H_2SO_4 was prepared by dilution of concentrated HCl and H_2SO_4 with distilled water and all experiments were carried out in unstirred solutions and all weighing were done with ADAM PGW – 253e digital analytical balance.

Preparation of A. paniculata root extract

The roots of *A. paniculata* were collected from the local bush in Nigeria. They 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 over 15 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 and stored (Okafor *et al.*, 2012; Uwah *et al.*, 2012 and Oguzie, 2006). 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.

Weight loss measurements

Weighed test specimens were fully immersed separately for 10 hours in each of the beakers containing the 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 1.0 M H_2SO_4 acid. Each of the test specimens was taken out every two hours, washed with distilled water, rinsed with ethanol, dried with acetone and re-weighed. Plots of weight loss against exposure time were made and corrosion rates were obtained and subsequently inhibition efficiency obtained from the equation (1) and (2):

$$\theta = 1 - \frac{W1}{W2} \quad (1)$$

$$IE\% = \theta \, x \, 100 \quad (2)$$

where θ is the surface coverage, W_1 is the corrosion rate of the blank, W_2 is the corrosion rate of the inhibitor, IE % is the inhibition efficiency (Singh *et al.*, 2010)

Hydrogen evolution measurements

In monitoring corrosion studies using this hydrogen evolution technique, 100 mL of the corrodent (1.0 M HCl) was introduced into the volumetric flask and the initial volume of the air

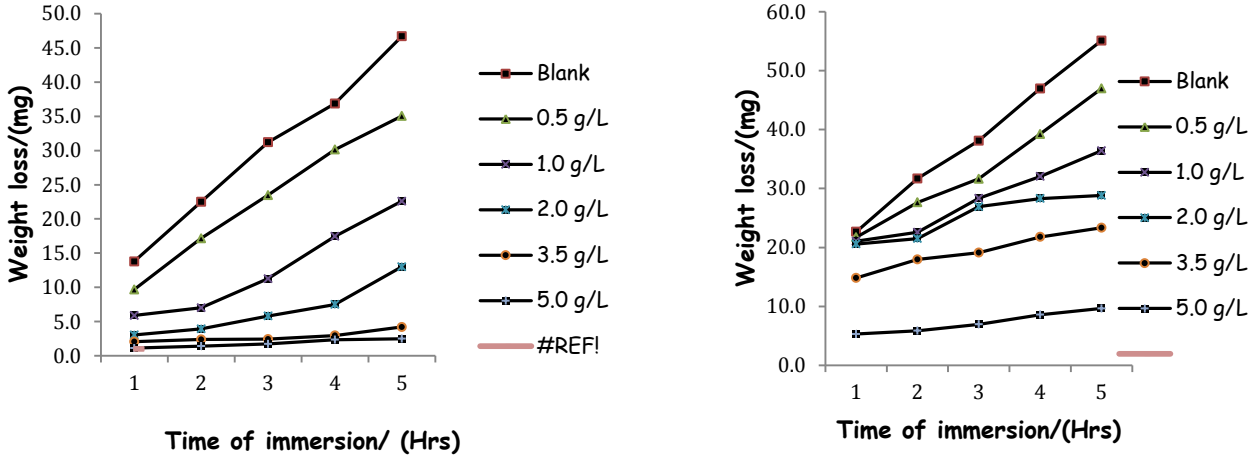
burette was noted. Thereafter, a mild steel coupon of dimension 1.20 cm x 0.08 cm x 4.00 cm already weighed was dropped into the pure acid solution and the flask was quickly closed. The volume of the hydrogen gas evolved from the corrosion reaction was monitored by volume changes in the level of paraffin oil in the graduated burette every minute for 30 minutes. In another experiment, a set of fresh specimens were immersed in the flask containing the corrodent at different concentrations each of *A. paniculata* root 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. The process above was repeated for the 1.0 M H_2SO_4 stock solution. Each experiment was repeated twice to ensure reproducibility, and the average values were recorded (Obot *et al.*, 2011 and Odiongenyi *et al.*, 2008).

Results and Discussion

Analysis of results from gravimetric measurements

The results obtained for the variation of weight loss with exposure time for the mild steel test specimen immersed in the two test media – 1.0 M HCl and 1.0 M H_2SO_4 are presented in Figures 1a and 1b.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 (Chetouani and Hammouti, 2003; Buchweishaja *et al.*, 2008). More loss of weight for the test specimens was, however, observed in the test in which there was no *A. paniculata* root extract addition (Chetouani and Hammouti, 2003; Gunasekeran and Chauhan, 2004). The mild steel reacted with HCl to displace hydrogen. The solubility of mild steel decreases with increasing time of exposure, hence the gradual setting in of passivation as compared with the that formed by H_2SO_4 (Loto, 2011 and Hsu *et al.,* 2004).

However, weight loss of mild steel was also found to decrease with an increase in the concentration of *A. paniculata* root extract indicating that the extract retarded the rate of corrosion of mild steel in solutions of HCl and H_2SO_4 (El-Etre *et al.*, 2005; Okafor *et al.,* 2007, Uwah *et al.*, 2013) as indicated in Table 1. Surface coverage (θ) and inhibition efficiency (IE %) increased with increase EEAPR concentration, this indicates that



(a) (b)

Figure 1: Variation of weight loss with immersion time for Mild steel in (a) 1.0 M HCl and (b) 1.0 M H_2SO_4 solutions in the presence and absence of *A. paniculata* root.

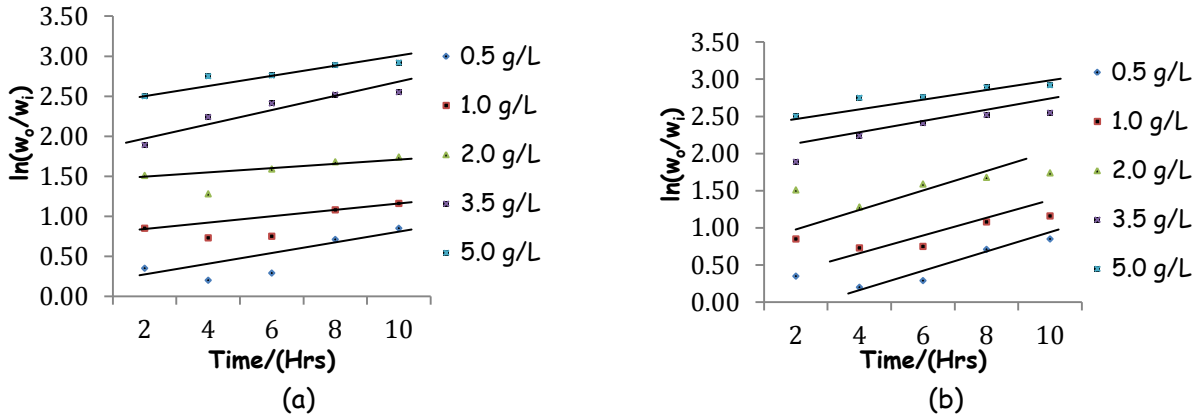


Figure 2: Variation of ln (w_o/w_i) with immersion time for Mild steel in (a) 1.0 M HCl and (b) 1.0 M H_2SO_4 solutions in the presence of *A. paniculata* root.

the corrosion of the metal has been inhibited and a larger fraction of the surface is protected against acidic attack at high inhibitor concentrations (El-Etre *et al.*, 2005; Okafor *et al.*, 2007; Uwah *et al.*, 2013, Ebenso *et al.*, 2008).

Analysis of results from hydrogen evolution measurements

The following mechanism can be proposed for hydrogen evolution reaction on electrodes in acidic media (Uwah *et al.*, 2013, Okafor *et al.*, 2007):

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 onto the electrode surface to produce hydrogen atom in acidic solution and adsorbed hydrogen atom, MH_{ad},

Table 1: Corrosion rates, surface coverage and inhibition efficiency for Mild steel sample in 1.0 M HCl and H_2SO_4 in the absence (blank) and presence of EEAPR.

	EEAPR in HCl solution			EEAPR in H_2SO_4 solution		
System	CR (mg/cm^2/hr)	θ	IE %	CR (mg/cm^2/hr)	θ	IE %
(Blank)	11.175	-	-	11.175	-	-
0.5 g/L	5.361	0.520	52.0	6.018	0.462	46.2
1.0 g/L	2.111	0.811	81.1	4.498	0.599	59.9
2.0 g/L	1.763	0.842	84.2	4.487	0.598	59.8
3.5 g/L	0.394	0.965	96.5	1.966	0.824	82.4
5.0 g/L	0.124	0.989	98.9	0.563	0.950	95.0

EEAPR - ethanol extract of Andrographis paniculata, CR –, Corrosion rate, θ – Surface coverage, IE- Inhibition Efficiency

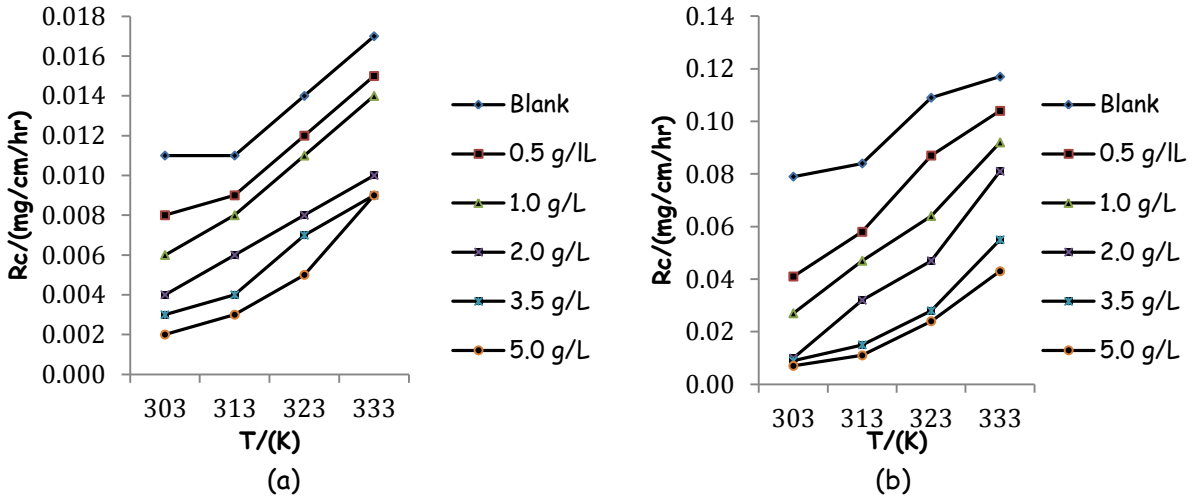


Figure 3: Variation of R_c with temperature (K) of Mild steel in the presence and absence of extracts of *A. paniculata* root in (a) 1.0 M HCl and (b) H_2SO_4 solution

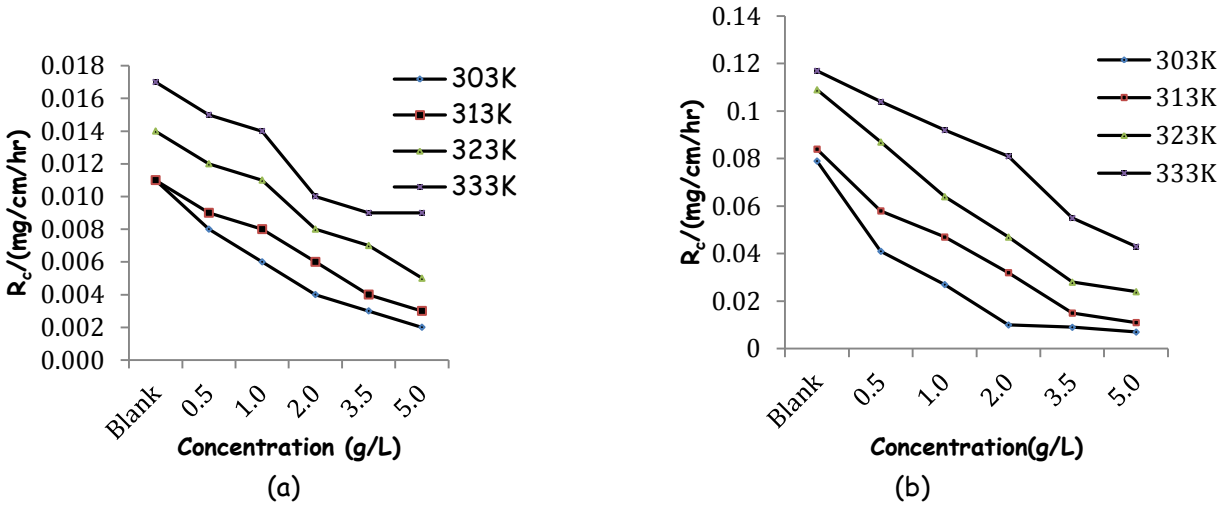


Figure 4: Variation of R_c (mg/cm^2/hrs) with concentration (g/L) of mild steel in the presence and absence of extract of *A. paniculata* root in (a) 1.0 M HCL and (b) H_2SO_4 solution.

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) (Loto, 2011). In spite of three states for the formulation of the mechanism, no one of the three reactions formulated occurs as a single step but combined with another. The results obtained however showed that the corrosion rate decreased with increase in the EEAPR concentrations, but increased with increase in temperature for both HCl and H_2SO_4 solutions (Figures 3 and 6). From the corrosion rates, the inhibition efficiency was determined using equation 2 (Loto, 2011). It is observed that inhibition efficiency increases with increase in extract concentration as well as decrease with increase in temperature for EEAPR in both acid solutions (Figures 5 and 6). This suggest that, fractions of *A. paniculata* root are adsorbed on the metal surface thereby protecting metal from the action of corrodent and the latter suggest a desorption phenomenon following weak forces of

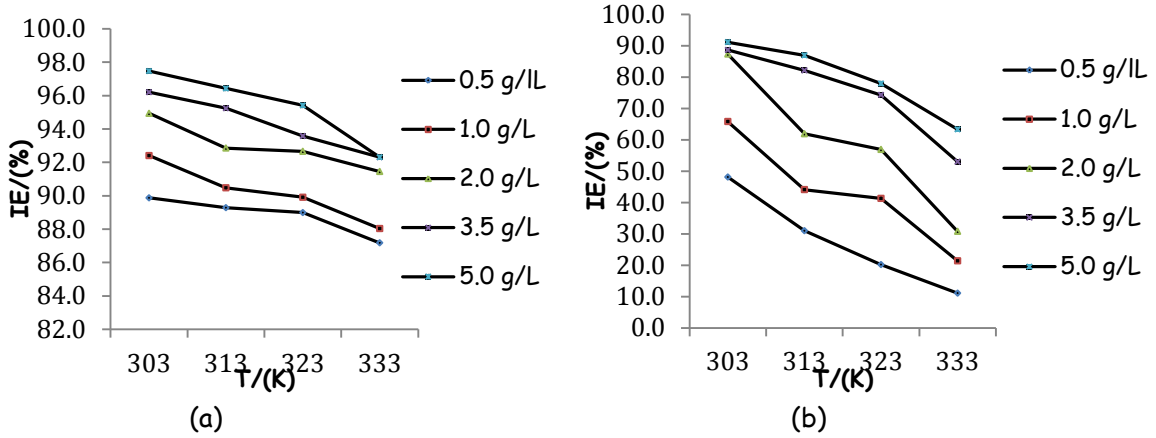


Figure 5: Variation of IE (%) with temperature (K) of Mild steel in the presence and absence of extracts of *A. paniculata* root in (a) 1.0 M HCL and (b) 1.0 H_2SO_4 solution.

attraction due to high temperature effects. This is in agreement with the observation of other workers (Chetouani and Hammouti, 2003; Oguzie, 2007 and Gunasekaran and Chauhan, 2004). The trend in temperature suggests physical adsorption respectively.

Thermodynamic and Kinetic data

Values of standard free energy of adsorption, ΔG^*_{ads} were obtained from the reciprocal of the intercept of Fig. 9. The constant k is related to standard free energy of adsorption by the equation 3 (El-Etre *et al.*, 2005 and Obot *et al.*, 2011)

$$k = \frac{1}{55.5}\exp\frac{-\Delta G_{ads}}{RT} \qquad (3)$$

The calculated ΔG^*_{ads} values are listed in Table 3. The negative values of adsorption free energy indicate that the adsorption of the inhibitor molecules is a spontaneous process (Okafor *et al.*, 2012; Uwah *et al.*, 2012; Oguzie, 2006 and Fatemeh *et al.*, 2012). The ΔG^*_{ads} for the inhibition of mild steel were found to be between -15.9 & -17.7 and -15.6 $KJmol^{-1}$ &-14.5 $KJmol^{-1}$ in 1.0 M HCl and 1.0 M H_2SO_4 solutions of the extract respectively.

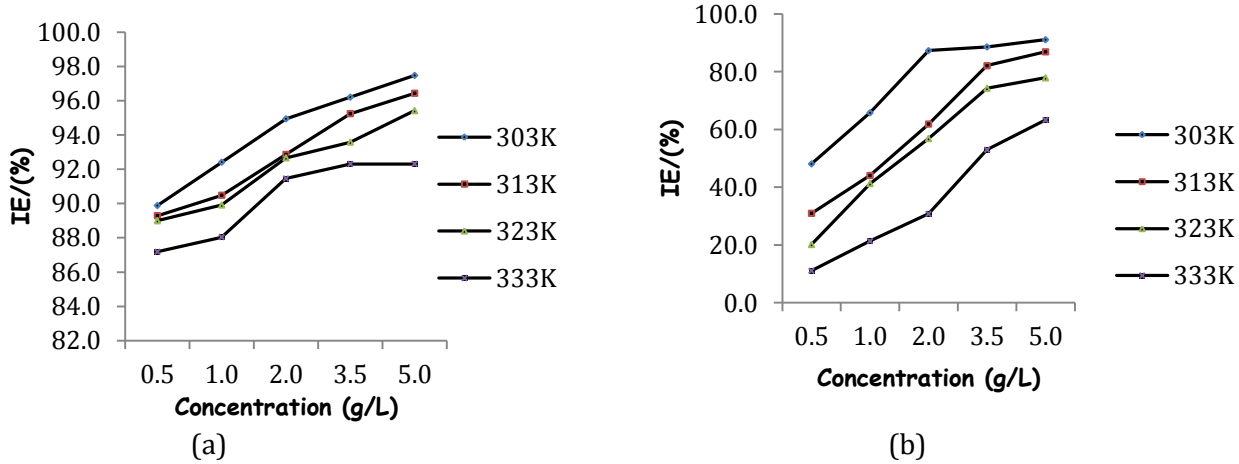


Figure 6: Variation of IE (%) with Conc. (g/L) of Mild steel in the presence and absence of extracts of *A. paniculata* root in (a) 1.0 M HCl and (b) H_2SO_4 solution.

The observed ΔG^*_{ads} values (Table 3) support the mechanism of physisorption for the inhibitor's action in both acid media following the fact that ΔG^*_{ads} values greater than -42KJmol^{-1}denotes physisorptions. In examining the effect of temperature on the corrosion inhibition process, the apparent activation energy (Ea) was calculated from the Arrhenius equation (4) (Bendahou *et al.*, 2006) and plots in Figure 7.

$$log\frac{Ra}{Rb} = \frac{Ea}{2.303R}\ \frac{1}{T1} - \frac{1}{T2} \qquad (4)$$

where Ra and Rb are the corrosion rates at temperature T1 and T2 respectively, and R the molar gas constant. Increased activation energy (Ea) in inhibited solutions compared to blank suggest that the inhibitor is physically adsorbed on the corroding metal surface while either unchanged or lower Ea values in the presence of inhibitor suggest chemisorptions (Subhashini, 2004 and Zuo *et al.*, 2004). It is seen from Table 2 that Ea values were higher in the presence of *A. paniculata* leaf extract in both 1.0 M HCl and H_2SO_4 acid solutions compared to that in their absence leading to an increase in their corrosion rates. It has been suggested 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 (Okafor *et al.*, 2005; Okafor *et al.*, 2008 and Okafor *et al.*, 2012; Uwah *et al.*, 2013 and Odiongenyi *et al.*, 2008). The Ea values support the earlier proposed physisorption mechanism. The negative values of $\Delta H°$ indicate that the dissolution of the metal is an exothermic reaction. This also suggests that mild steel dissolution requires more energy in 1.0 M HCl than H_2SO_4 in the presence of root extract (Fatemeh *et al.*, 2012; Loto, 2011; Rajam *et al.*, 2013; Chetouani and Hammouti, 2003; Oguzie, 2007 and Gunasekaran and Chauhan, 2004). The change in entropy ($\Delta S°$) was found to be greater than zero. This indicates that the reaction is irreversible. It is clear that, the complete desorption of the inhibitor is not possible in both acid media. The shift towards negative values of entropy ($\Delta S°$) imply that the activated complex in the rate determining step represents association rather than dissociation, meaning that disordering

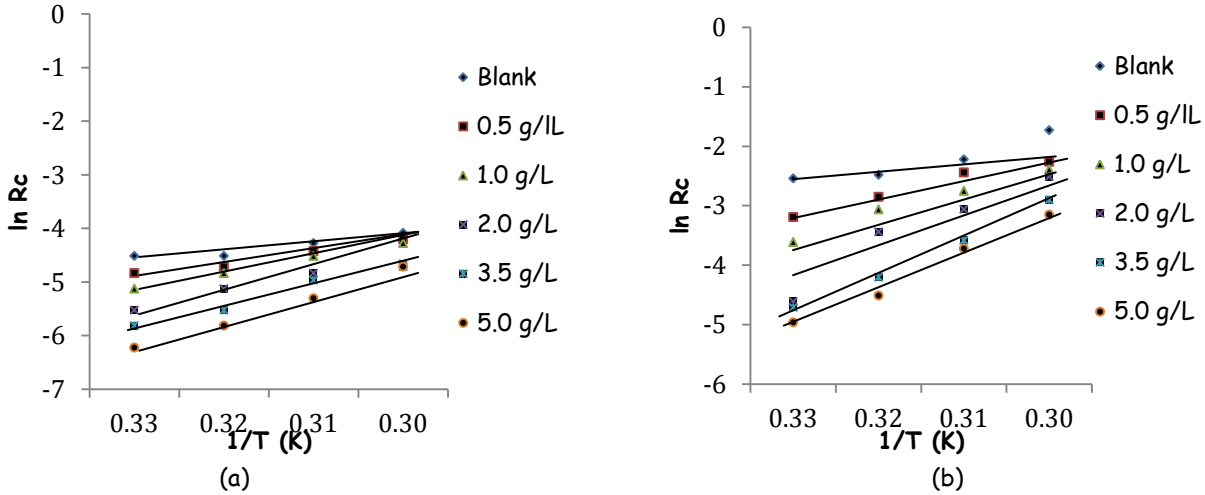


Figure 7: Arrhenius plots for Mild steel in (a) 1.0 M HCl and (b) 1.0 M H_2SO_4 solutions in the absence and presence of ethanol extract of *A. paniculata* root.

Table 2: Thermodynamic parameters for mild steel in 1.0 M HCl and H_2SO_4 in the absence and presence of the plant extracts

	Extract in HCl solution			Extract 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	-44.0	26.61	24.0	-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	41.9	39.2	-81.6	84.51	49.1	-110.0

Ea- Activation energy, ΔH^*_{ads} – Enthalpy of Adsorption, ΔS^*_{ads} – Entropy of Adsorption

Table 3: Adsorption parameters for Mild steel in 1.0 M HCl and H_2SO_4 solutions containing EEAPR using hydrogen evolution technique

	EEAPR in HCl solution				EEAPR in H_2SO_4 solution			
Temp (K)	Equi. Cons K (g/L)	ΔG^*_{ads} KJ/mol	R^2	slope	Equi. Cons K (g/L)	ΔG^*_{ads} KJ/mol	R^2	slope
303	10.1	-15.9	0.967	1.174	8.85	-15.6	0.948	1.133
313	10.2	-16.5	0.968	1.187	5.41	-14.9	0.979	1.028
323	10.4	-17.1	0.967	1.201	4.74	-15.0	0.910	1.011
333	10.8	-17.7	0.965	1.238	3.42	-14.5	0.934	0.682

EEAPR - ethanol extract of Andrographis paniculata, Temp – Temperature, Equi. Cons – Equilibrum Constant, ΔG^*_{ads} – Free Energy of activation

Table 4: Kinetic data for EEAPR in 1.0 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

decreases on going from reactants to the activated complex according to (El – Etre *et al.*, 2005 and Oguzie, 2005**)**.

$$log\frac{CR}{T} = log\ \frac{R}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (5)$$

The kinetics of the dissolution of mild steel 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 root extract was studied by fitting the corrosion data into different rate laws (Okafor *et al.*, 2005; Okafor *et al.*, 2008; Okafor *et al.*, 2012; Oguzie, 2007; Singh *et al.*, 2010; Singh *et al.*,2011 and Singh *et al.*,2012). As presented in Figure 2, the corrosion data fitted well first order kinetic model formulated in equation (6).When $\ln(W_o/W_i)$ was plotted versus time, a linear variation obtained indicated first- order reaction kinetics in both HCl and H_2SO_4 solutions in the absence (blank) and present of each of the five different inhibitor concentrations (Fig. 2).

$$ln\frac{Wo}{Wi} = -kt \qquad (6)$$

where k is the rate constant. This result (Fig. 2 and Table 4) suggests an inhibition of the dissolution process without affecting the reaction order (Obot *et al.*, 2011; Odiongenyi *et al.*, 2008; Okafor *et al.*, Okafor *et al.*,2008 and Uwah *et al.*, 2013).

Adsorption consideration

Values of surface coverage (Θ) were tested graphically with different isotherms (James and Akaranta, 2009; Singh *et al.*, 2011; Singh *et al.*, 2012; Zuo *et al.*, 2004 and Rajam *et al.*, 2013). As shown in Fig. 9, a straight line is

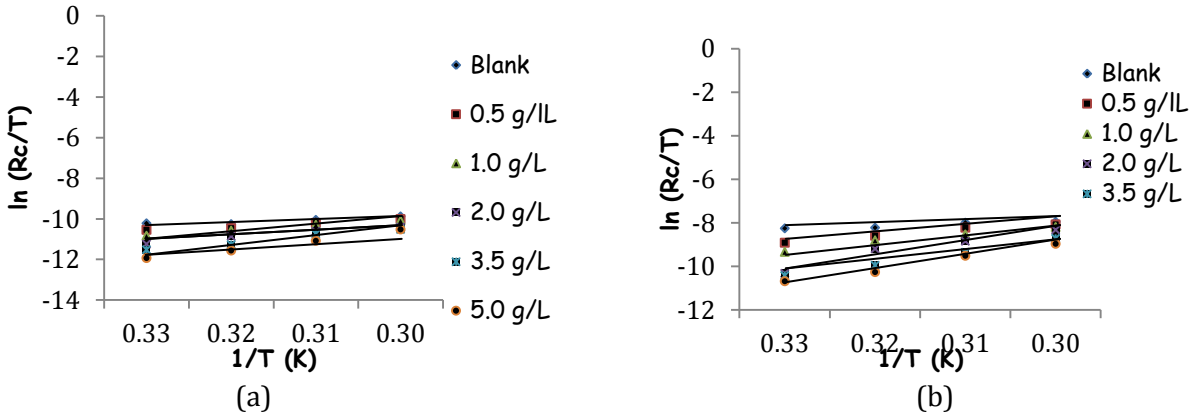


Figure 8: Eyring transition state plots for Mild steel in (a) 1.0 M HCl and (b) 1.0 M H_2SO_4 solutions in the absence and presence of EEAPR

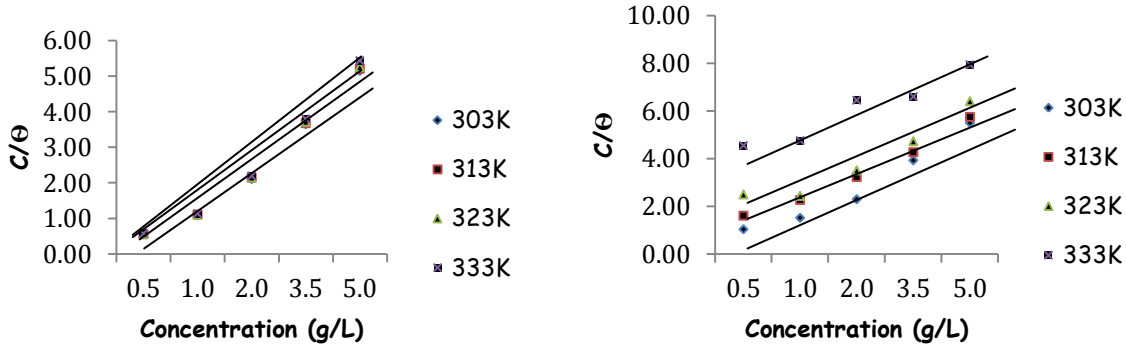


Figure 9: Langmuir adsorption isotherm for mild steel samples in (a) 1.0 M HCl and (b) 1.0 M H_2SO_4 solutions containing EEAPR

obtained for the *A. paniculata* root extract in both HCl and H_2SO_4 acid solutions, when C/Θ is plotted against C, and the linear correlation coefficients of the fitted data are good (Table 3). This indicates that the adsorption behavior is consistent with Langmuir's adsorption isotherm (Singh *et al.*, 2010; El – Etre *et al.*, 2005 and Subhashini, 2004), expressed as equation 7:

$$\frac{C}{\theta} = \frac{1}{Kads} + C \qquad (7)$$

where Θ is the degree of surface coverage, k the equilibrium constant of the adsorption process and C the concentration of the inhibitor in the electrolyte (Oguzie, 2005; Oguzie *et al.*, 2007; Okafor *et al.*, 2007 and Uwah *et al.*, 2012).

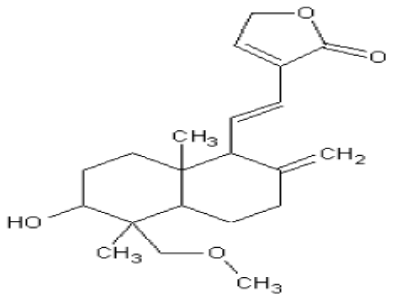


Figure 10: Structure of Andrographolide

Mechanism of inhibition

The main constituent of *Andrographis paniculata* root extracts is Andrographolide (a bicyclic diterpenoid lactone) that contributes to the corrosion inhibition. The structure is given in Fig. 10. (Singh *et al.,* 2010). This structure has multiple bonds through which they get adsorbed on the mild steel surface. This plant also contain major constituent known as flavonoids which is also an important compound that proffers antioxidant activity. The performance of *Andrographis paniculata* root extracts could also be due to large size of constituent's molecules which cover wide areas on the metal surface and thus retarding the corrosion (Obot *et al.*, 2011 and Singh *et al.*, 2010). *Andrographis paniculata* root extract are composed of numerous naturally occurring organic compounds. The inhibitive action of *Andrographis paniculata* root extract towards the acid corrosion of mild steel can be attributed to the adsorption of root extract components onto the steel surface. This root extract contain oxygen atoms in functional group and aromatic ring, which meets the general consideration of typical corrosion inhibitors.

Table 5: Phytochemical screening of the ethanol extracts of *Andrographis paniculata* root

Chemical constituents screening	A. paniculata root
Akaloids	+
Saponins	-
Flavonoids	+
Tannins	+
Polyphenols	+
Anthraquinones	-
Lactones	+
Glucosides	-
Antioxidants	+
Farnesols	+

(+) - Present, (-) - Absent

Conclusion

1. The highest valuable results for corrosion inhibition performance in the HCl test medium was achieved at the *A. paniculata* root extract concentrations of 5.0 g/L (98.9%) at 333K.

2. In the sulphuric acid test medium, the highest appreciable result was achieved also at 5.0 g/L (95.0%) at the elevated temperature of 333K.

3. The performance of the extract in the two test media was weak after about 10 hours; as the inhibitor efficiency was also low.

4. The two acid test media – HCl and H_2SO_4, at the concentration of 1.0 M were clearly too strong to maintain stable inhibiting film adsorption on the metal specimens' surface, particularly at the elevated temperature(s) with the concentrations of the *A. paniculata* root extract used.

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