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Research Article

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Alkaloids Extract from *Peganum harmala* Plant as Corrosion Inhibitor of 6063 Aluminium Alloy in 1 M Hydrochloric Acid Medium

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ABSTRACT

The inhibitory action of alkaloids extract from Peganum harkmala (AEPH) on the corrosion of 6063 aluminium alloy in 1 M HCl solution has been investigated by weight loss and potentiodynamic polarization technique. The efficiency was found to increase with increasing concentration of the plant extract. The results obtained showed the extract solution of the plant could serve as an effective inhibitor for the corrosion of 6063 aluminium alloy in hydrochloric acid solution. 91.78% is the maximum inhibition efficiency obtained from potentiodynamic polarization technique with 25mg/l of the alkaloids extract at 25°C. The effect of temperature on the corrosion behavior of 6063 aluminum alloy in 1 M HCl with and without addition of alkaloid extract (AEPH) was studied in the temperature range 298–313K by weight loss technique. The adsorption process follows Langmuir adsorption isotherm.

Keywords: Alkaloids; *Peganum harmala* extract; Acid solutions; Corrosion; Aluminium

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INTRODUCTION

Aluminum alloys are used in engineering design chiefly for their light weight, corrosion resistance. They are also utilized for their high electrical and thermal conductivities, ease of fabrication, and ready availability. The corrosion resistance of aluminum is dependent upon a protective oxide film [1]. This film is stable in aqueous media when the pH is between about 4 and 8,5. When aluminum is exposed to aggressive environments such as acid pickling solutions, chemical etching, industrial cleaning or scale dissolving, these processes lead to corrosion of aluminum [2]. Corrosion of aluminum and its alloys is one of the most important problems which reduce their extended life. In order to prevent and minimize aluminum dissolution, different corrosion inhibitors are used [3,4]. Despite the large number of suitable inhibitors to prevent corrosion of metal, the discovery and development of novel corrosion inhibitors is required, because a lot of known and used inhibitors are dangerous to the environment and human health [5,6]. The use of inhibitors is one of the best known methods of corrosion protection. A large number of organic compounds, particularly those containing nitrogen, oxygen or sulphur in a conjugated system, are known to be applied as inhibitors to control acid corrosion of iron, steel and aluminum. Several researchers studied the effect of natural products as corrosion inhibitors in different media [7-9]. Many plants are known produce various types of alkaloids as Aspidosperma album [10] Annona squamosa [11] Palicourea guianensis [12] Neolmarckia cadamba [13] Garciana Kola [14] Siparuna guianensis [15]. But studies on the use of alkaloid extract Harmal as a corrosion inhibitor for aluminum and its alloys is unknown. Harmal alkaloids are β-carboline system derivatives which frequently occur in the indole alkaloid series. Harmine and harmaline are the main alkaloids of *Peganum harmala* L. The aim of this study is to investigate the inhibition effect of the alkaloids extract of *Peganum harmala* L. (Syrian rue), on the corrosion of 6063 aluminum alloy in 1 M HCl solution by weight loss and potentiodynamic polarization.

EXPERIMENTAL SECTION

Extraction and isolation of alkaloids from *Peganum harmala* L

The grains of the *Peganum harmala* L, dried then crushed in the form of powder. 5g of the latter is soaked 4fois with 50 ml of methanol in 50 °C in the bath marry during 1 hour. Extracts were combined and birdbrains dry. The residue was dissolved in HCl 1N in a 2 % concentration then filtered. The filtrate was twice extracted with 20 ml from ether of oil. The aqueous phase of acid was made basic (pH = 10) with NaOH 1N. The neutralized phase is four times extracted with 50ml of chloroform. The phase of chloroform was combined and birdbrains dry, then the residue was dissolved in 25 ml of methanol. The solution of extracted alkaloid was got through filter of 0,45 µm and stored in 4°C refrigerator for a later use [16].

Aggressive solutions

The aggressive solutions of 1.0 M HCl was prepared by dilution of AR grade 37% HCl and with distilled water. The stock solution (1000 mg. l^{-1}) of alkaloids was used to prepare the desired concentrations by dilution with distilled water. The concentration range of alkaloids extract from *Peganum harmala* L used was 10–50 mg l^{-1}.

Weight loss test

Tests were performed on aluminum specimens (Al 6063) with the following chemical compositions (wt %): (Table 1)

Table 1: Chemical composition of the aluminum alloys (Al 6063) [17]

Al %	Mg%	Si%	Mn%	Fe%	Zn%	Cu%	Ti%	Ni%	Cr%
Balance	0.53	0.4	0.04	0.2	<0,002	<0,03	<0,002	<0,003	<0,002

Weight loss tests were conducted under total immersion in 20 ml of 1.0 M HCl media at 298K controlled by a water thermostat. Three parallel aluminum sheets of 2.5cm x 2cm x 0.20 cm were abraded by a series of emery paper (grade 320 to 1200) and then washed with distilled water and acetone. After weighing by digital balance with sensitivity of ±0.1 mg, the specimens were suspended in a beaker containing test solutions using glass hooks and rods. After immersion for 3 h, the specimens were taken out, washed with bristle brush under running water in order to remove the corrosion product, dried with a hot air stream, and re-weighed accurately. The mean weight loss of three parallel aluminum sheets can be obtained, and then the corrosion inhibition efficiency (IE%) is calculated [18-24], using the following equation:

$$IE\% = \frac{W_0 - W_1}{W_0} \times 100 \qquad (1)$$

Where, W_0 and W_1 are the weight loss of the aluminium alloys in the absence and presence of inhibitor, respectively.

Polarization measurements

Electrochemical experiments were carried out in the conventional three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE). The working electrode is of cylindrical shape with an area of 0.5cm^2. This shape is preferred, because it assures a greater surface and a reduce number of edges. Prior to each test, the working electrode was polished with emery paper of varied 320 to1200, degreased in acetone at room temperature in order to remove all traced of fat and remained abrasive powder on the electrode surface after polishing. After that, the working electrode was washed with distilled water and inserted in the polarization cell, which was the usually three-electrode cell.

All electrochemical measurements tests have been performed at 25°C under atmospheric oxygen without agitation out using a voltalab pgz100. The potential of potentiostatic polarization curves was started from a potential of -1000 mV to +1500 mV versus at a sweep rate of 10 mV s^{-1}. Inhibition efficiency (IE%) is calculated through the corrosion current density values (i_{corr}) [25].

$$\mathrm{IE\%} = \frac{\mathrm{I_0} - \mathrm{I_1}}{\mathrm{I_0}} \times 100 \qquad (2)$$

Where, I_0 and I_1 are the corrosion current density of the aluminium alloy in the absence and presence of inhibitor, respectively.

RESULTS AND DISCUSSION

Weight loss measurements

The values of inhibition efficiency (IE%) obtained from the weight loss after immersion for 3 h for different extract concentrations (10–50 g l^{-1}) in 1.0 M HCl at 298K,303K and 313K are shown in Figure 1. It is found that IE% increases with the increase in concentration at 298K. The maximum value is 86% for 25ppm. These results indicate that alkaloids are a good inhibitor for aluminum in 1.0 M HCl. (Table 2)

Table 2: Results of Weight loss measurements studies on 6063 aluminium alloy in 1M hydrochloric acid containing different concentrations of inhibitor AEPH

T(K)	AEPH C(mg/l)	Log C_{inh} (mg/l)	Corrosion rate mg cm^{-2} h^{-1}	Log C_R (mg cm^{-2} h^{-1})	% IE Weight loss	θ	C/θ (mg/l)	log (θ/1-θ)
298K	0	-	1.38	0.14	-	-	-	-
	10	1	0.347	-0.46	74.88	0.7488	13.35	0.473
	15	1.18	0.253	-0.595	81.64	0.8164	18.373	0.647
	20	1.3	0.2	-0.699	85.51	0.8551	23.389	0.76
	25	1.4	0.193	-0.716	86	0.86	29.073	0.791
303K	0	-	1.833	0.263	-	-	-	-
	10	1	0.74	-0.131	59.64	0.5964	16.728	0.17
	15	1.18	0.627	-0.203	65.82	0.6582	22.789	0.287
	20	1.3	0.573	-0.242	68.72	0.6872	29.104	0.343
	25	1.4	0.553	-0.257	69.82	0.6982	35.806	0.365
313K	0	-	4.84	0.685	-	-	-	-
	10	1	3.427	0.535	29.16	0.2916	34.3	-0.387
	15	1.18	3.273	0.515	32.34	0.3234	46.4	-0.321
	20	1.3	3.153	0.498	34.85	0.3485	57.39	-0.274
	25	1.4	2.8	0.447	42.14	0.4241	59.32	-0.139

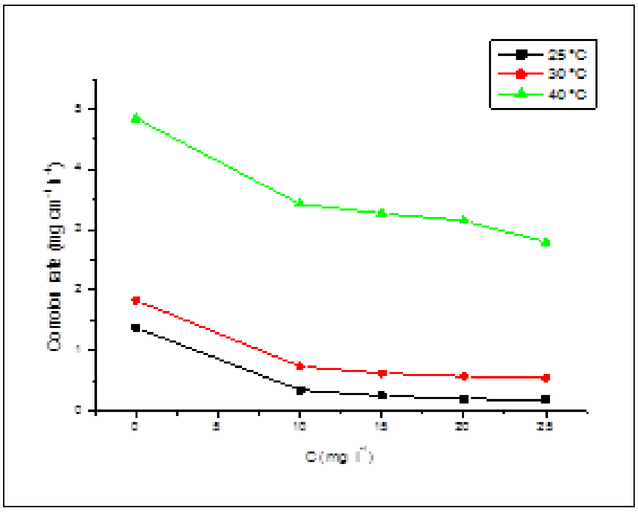

Figure 1: Weight loss expressed as the corrosion rate (mg cm^{-2} h^{-1}) for 6063 aluminium alloy in 1 M HCl solution containing different concentrations of alkaloids extract from *Peganum harmala* L after 3h of immersion at 298K, 303K and 313

Polarization curves

The Tafel polarization curves 6063 aluminum alloy in 1.0 M hydrochloric acid solutions at different concentrations of inhibitor at 298K is present in the following figure (Figures 2 and 3).

The potentiodynamic parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c and b_a), corrosion current density (i_{corr}), were obtained from Tafel plots and the inhibition efficiency values (IE%), were calculated using equation 2. The results are tabulated in Table 3.

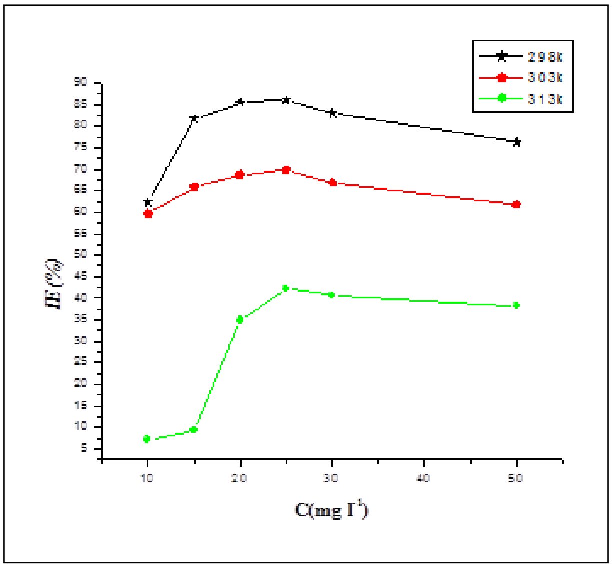

Figure 2: Plots of Relationship between inhibition efficiency (IE%) and concentration of alkaloids extract from Peganum harmala L in 1.0 M HCl (weight loss method, immersion time is 3h) at 298K,303K and 313K

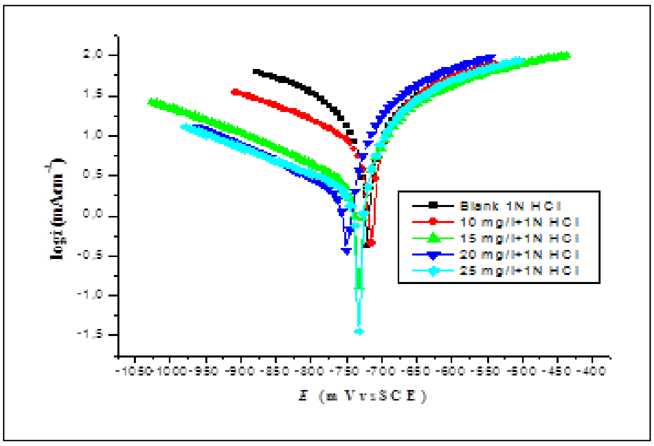

Figure 3: Tafel polarization curves of 6063 aluminum alloy in 1.0 M HCl without and with different concentrations of AEPH at 25°C

Table 3: Results of Tafel polarization studies on 6063 aluminium alloy in 1.0 M hydrochloric acid containing different concentrations of inhibitor

Concentration mg L^{-1}	**E_{corr}**	**I_{corr}**	**ba**	**bc**	**Rp**	**IE** Icorr	**IE**
	(mV)	**(μAcm^{-2})**	**(mV dec^{-1})**	**(mV dec^{-1})**	**(Ω cm^2)**	**(%)**	**(%)**
Sans inhibiteur	-719.3	23.9289	351.6	-383	2.3	-	-
10	-715.7	6.6003	94.9	-220.6	7.89	72.82	71
15	-741.8	4.2094	116	-356.9	13.38	82.4087	82
20	-774	2.4759	90.5	-259.8	19.05	89.65	88
25	-746.3	2.249	79.1	-313.9	20.95	90.6	89
50	-744.7	3.0413	81.6	-239.1	12.93	86.72	82

From Figure 3 and Table 3, it can be observed that the addition of alkaloids extract Peganum Harmala, at all the studied concentrations resulted in the significant decrease in the corrosion current density (i_{corr}) and decrease in the corrosion rate. It is also evident that percentage efficiency of the inhibitor increased with increase in the concentration of the inhibitor. There was no remarkable shift in the corrosion potential (Ecorr) value with respect to the without inhibitor. Both anodic and cathodic polarizations are influenced simultaneously, almost to the same extent, which indicate the influence of CSE on both the anodic and the cathodic reaction. According to literature report [26-31], when corrosion potential is more than -85 mV with respect to the corrosion potential of the without inhibitor, the inhibitor can be considered as either cathodic or anodic type. However, the maximum displacement in this study is less than -85 mV. This suggests that CSE functions as mixed-type inhibitor

Adsorption isotherm

For the present study, the adsorption of *Peganum harmala* L on 6063 aluminium alloy surface obeys Langmuir adsorption isotherm:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (3)$$

Where C is the concentration of inhibitor, K the adsorptive equilibrium constant and θ is the surface coverage with the value of inhibition efficiency (IE%).The linear regressions between C/θ and C at different temperature were calculated, and the corresponding parameters are listed in Table 4. Figure 4 shows the straight lines of C/θ versus C at 298K.

Table 4: Thermodynamic parameters from Langmuir adsorption isotherm of corrosion of 6063 aluminium alloy in 1.0 M hydrochloric acid containing different concentrations of inhibitor

T	K_{ads} (l g^{-1})	ΔG°_{ads} (kjmol^{-1})	1000/T (K)	lnK (K)	ΔH° (kjmol^{-1})	ΔS° (kjmol^{-1}K^{-1})
298	363	-24,53	3,36	5,89	-103,62	-0,256
303	259	-24,12	3,3	5,56	-103,62	-0,256
313	52	20,73	3,2	3,96	-103,62	-0,256

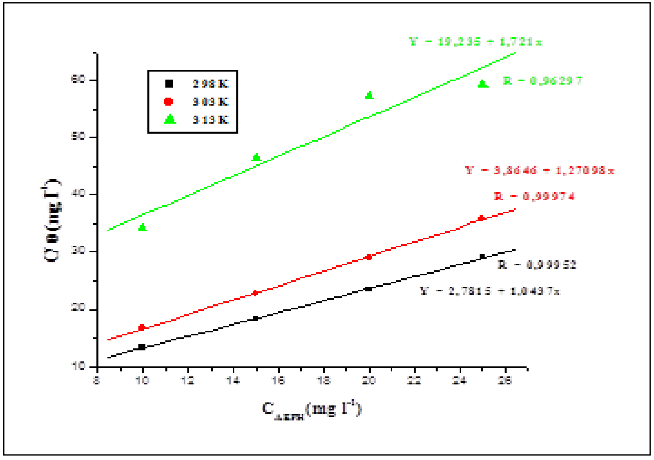

Figure 4: Langmuir adsorption plots for the aluminium corrosion in 1N HCl containing different concentrations of the alkaloids extract from Peganum harmala at 298, 303 and 313K using weight loss measurement ΔG

Recently some authors [32-40], in their study noted that discussion of the adsorption isotherm behavior using plant product extracts as inhibitors in terms of the standard free energy of adsorption value is not possible because the molecular mass of the extract components is not known. The standard adsorption enthalpy (ΔH°) is calculated on the basis of Van't Hoff equation:

$$dlnK/dT = \Delta H°/RT^2 \qquad (4)$$

Where R is the gas constant (8.314 J K^{-1} mol^{-1}), T the absolute temperature (K), and K is the adsorptive equilibrium constant. Eq. (5) can also be rearranged as the following equation [41]:

$$\ln K = (-\Delta H°/RT) + D \qquad (5)$$

Where D is integration constant.

The standard free energy of reaction, ΔG°_{ads} in kJ mol^{-1}, with the following equation [42]:

$$\Delta G^{\circ}_{ads} = - RT \ln (K_{ads} \times 55{,}5) \qquad (6)$$

Where 55.5 is the concentration of water in the solution in mol/l, R is the universal gas constant in J mol^{-1} deg^{-1} and T is the absolute temperature. The values of K_{ads} it is 2, 9674 .10^6 l/mol and the standard free energy of the reaction, ΔG_{ads} it is -36,33KJ/mol. Generally, if the values of $\Delta G°_{ads}$ are in the range up to -20 kJ/ mol, they are consistent with physisorption of the organic molecules or their protonated species on the surface. Inhibition is, therefore, due to electrostatic interaction between charged species and the charged metal, while those above -40 kJ/mol are associated with chemisorption as a result of sharing or transfer of electrons from organic species to the metal surface to form a metal bond [43-47]. With the obtained both parameters of ΔG° and ΔH°, the standard adsorption entropy (ΔS°) can be obtained using the following thermodynamic basic equation:

$$\Delta S° = (\Delta H°-\Delta G°)/T \qquad (7)$$

From the result, it was found that the experimental data fitted the thermodynamic-kinetic model of El-Awady et al. [48] (Figure 5). The model may be formulated as Eq. (8):

$$Log (\theta/1-\theta) = \log K' + y \log c \qquad (9)$$

Where c is the concentration of the adsorbate, θ is the coverage degree and 1/y is the number of inhibitor molecules occupying one active site. The binding constant K is given by:

$$K = K'^{(1/y)}$$

The efficiency of a given inhibitor is a function of both the magnitude of its binding constant K and the number of active sites (1/y) it is capable of blocking, with the former being the most important (El-Awady et al)[48]. Large values of K mean better and strong interaction, while small values of K mean that the interaction between the inhibitor molecules and the metal is weaker.

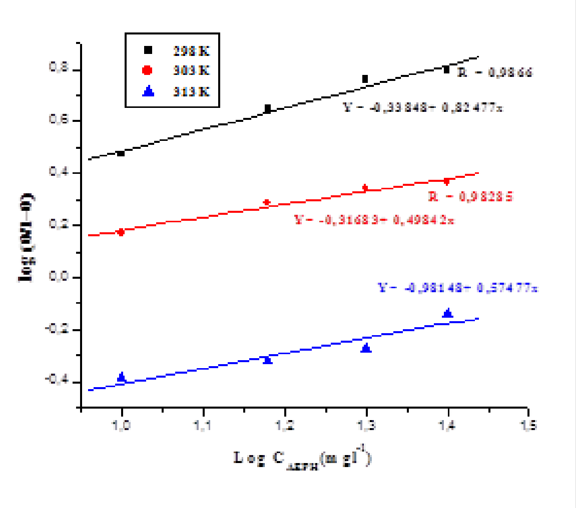

Figure 5: Thermodynamic-kinetic model for aluminium 6063 alloy in 1.0M HCl solutions containing alkaloids extract from Peganum harmala at 298, 303 and 313K (using weight loss technique)

The results obtained by the Langmuir isotherm and thermodynamic-kinetic model, the values of K and ΔG_{ads} calculated by Langmuir isotherm and 1/y, K and ΔGads calculated by the kinetic model are given in Table 4. The large values of ΔG_{ads} and its negative sign indicate that the adsorption of the second group compounds on aluminum 6063 surface is proceeding spontaneously and is accompanied by a highly efficient adsorption. It is noting that the value of 1/y is less than unity. This means that given inhibitor molecules will form multilayer on aluminum 6063 surface. In general the values of DG ads obtained from [48]. model are comparable with those obtained from Langmuir isotherms.

Effect of temperature on corrosion inhibition

The effect of temperature on the corrosion rate of 6063 aluminium alloy in 1 M HCl containing inhibitor at deferent concentration was studied in the temperature range 298–313 K using weight loss measurements during 3h, the corresponding results are summarized in Table 2. The results suggest that the extract was adsorbed on the 6063 aluminium alloy surface at all temperatures studied. The data in figure 6 indicate that the rates of 6063 aluminium alloy corrosion in the absence and presence of the extract increased with the rise in temperature in acid media. This is because an increase in temperature usually accelerates corrosive processes.

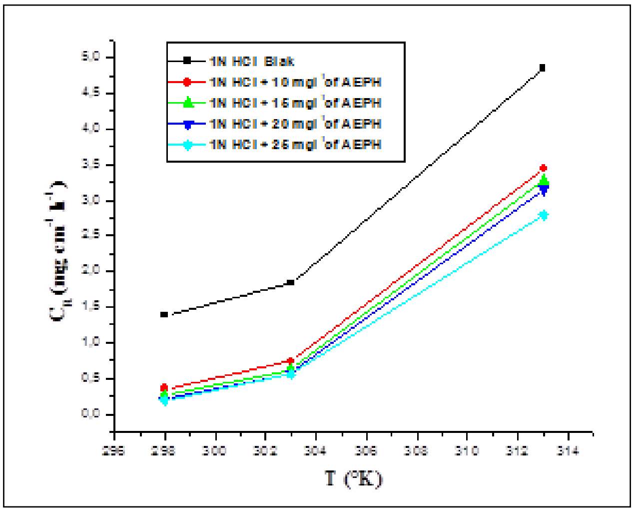

Figure 6: Corrosion rates of 6063 aluminium alloy in absence and presence of the alkaloids concentration increased with the rise in temperature in acid media

The activation parameters for the dissolution of 6063 aluminium alloy in 1 M HCl solutions in the absence and presence of AEPH were calculated from the Arrhenius-type plot (Eq. (6)) and the transition state Eq. (10):

$$I_{corr} = A\exp(-Ea/RT) \qquad (10)$$

$$I_{corr} = RT/Nh \exp(\Delta S°/R) \exp(-\Delta H°/RT) \qquad (11)$$

Where R is the universal gas constant, N is the Avogadro's number, h is the Plank's constant, Ea is the activation energy, T is the absolute temperature, and ΔH° and ΔS° are the standard enthalpy and entropy of activation, respectively.The apparent activation energy was determined from the slopes of Ln C_R versus 1,000/T graph depicted in (Figure 7) and the calculated activation energies obtained from the slopes of the plots (Figure 8) are listed in Table 3.

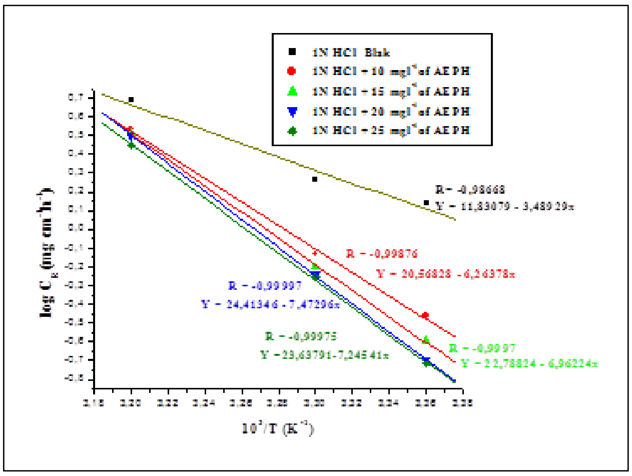

Figure 7: Arrhenius plots for the aluminium corrosion in 1N HCl containing different concentrations of the AEPH at 298,303 and 313K

Calculated values of activation energy, change in enthalpy and change in entropy for 6063 aluminium alloy in 1,0N HCl solutions containing different concentrations of the alkaloids extract from *Peganum harmala* (using weight loss technique).

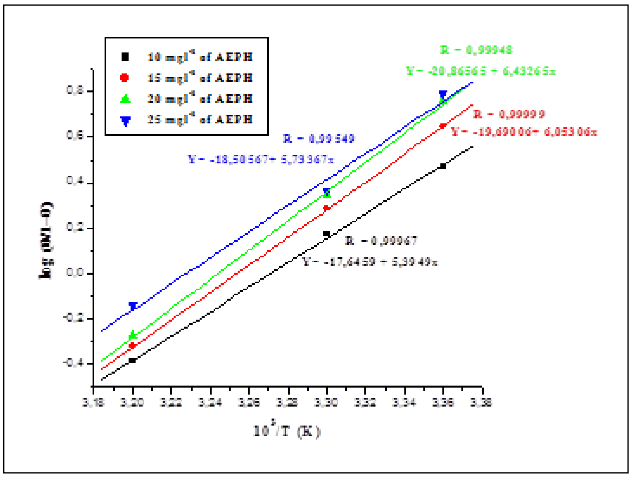

Figure 8: Plots of log (θ/1-θ) versus 1/T for the aluminium corrosion in 1N HCl containing different concentrations of the alkaloids extract from Peganum harmala at 298,303 and 313K

CONCLUSION

The alkaloids extract from Peganum Harmala (AEPH) were found to inhibit the corrosion of 6063 aluminium alloy in 1 M HCl solution. The inhibition efficiency increases with increase in concentration of alcaloids and with decrease in temperature suggesting physical adsorption. The inhibition is due to the adsorption of alkaloids on the surface of the metal. The experimental data obtained in this study fits the thermodynamic-kinetic model of El-Awady et al. (1992) adsorption isotherm.

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