Inhibitive Efficacy of *Citrullus Colocynthis* extract on the corrosion of aluminium alloy in sulphuric acid Medium

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Abstract :

Anti-corrosive propensity of ethanolic extract of *Citrullus colocynthis* fruit extract on aluminium alloy corrosion in 1N H_2SO_4 acid solution was investigated by weight loss technique at elevated temperature between 303-343 K. The inhibition efficiency (η%) has been observed significantly high (59.70 %) at 303 K at concentration 0.45 %. The adsorption of inhibitor on aluminium alloy surface have been found to obey Langmuir adsorption isotherm. It was observed to be physical, exothermic and spontaneous. The kinetic parameters such as activation energy (E_a), enthalpy of activation (ΔH_{act}), entropy of activation (ΔS_{act}) and thermodynamic parameters like free energy of adsorption (ΔG^0 ads), enthalpy of adsorption ($\Delta H^0{}_{ads}$), entropy of adsorption ($\Delta S^0{}_{ads}$) were calculated. These Kinetic and Thermodynamic parameters indicate a strong interaction among the inhibitor and metal surface. The high protective impact is attributed due to phytochemical ingredients present in the *Citrullus Colocynthis* fruit extract.

Keywords : Aluminium alloy, sulphuric acid corrosion, *Citrullus Colocynthis,* Langmuir adsorption isotherm, Thermodynamic and kinetic parameters.

1. INTRODUCTION

Aluminium alloy is applied broadly as a metal or alloy in numerous industrial applications. Acid solutions are applied in various industrial processes namely acid descaling and acid cleaning etc. Corrosion inhibitors are the substances added to the corrosive medium to reduce the rate of its attack on the metal or alloy [1] and these may be organic or inorganic compounds [2 - 4].

Numerous industries exploitation equipment made from metals under diverse circumstances ranging from mild to stiff chemical environments, making their surfaces susceptible to corrosion [5-6]. Investigation have shown that corrosion cannot be perfectly removed from metal surfaces owing to the various environments in which metals are applied [7]. Natural product of plant origin contains different organic compounds (viz – Alkaloids, Steroids, Amino acids, Tannins, Flavanoids etc.) and most are known to have inhibitive action [8-9].

Citrullus Colocynthis has very high medicinal value[10]. The plant contains three antitumor ingredients : cucurbitacin B , cucurbitacin E and D-glycoside of beta-sitosterol. The pulp contains colocynthin, a resinous substance insoluble in ether, gum, pectin, water and calcium and magnesium phosphates. Seeds contain the phyto-sterolin, two hydrocarbons, an alkaloid, glycoside, tannin βsitosterol, β-Carotene, terpenoids, steroids (sterols and bile acids), flavonoids, phenolic compounds and fatty acids etc. [11]. Inhibitive propensity is attributed owing to these phytochemical constituents present in the extract. *Citrullus Colocynthis* fruits extract is biodegradable and non-toxic therefore its applications would help to diminish the economic cost of corrosion monitoring as well as reduce the subsequent environmental threats.

A huge number of scientific studies have been devoted to the corrosion of aluminium and the exploitation of natural products as a corrosion inhibitors as *Tamarindus indica* [12], *Piper nigrum* [13], *Acacia nilotica* [14], *Azadirachta indica* [15] for aluminium in acidic media.

In the present study, the influence of elevation in temperature on inhibitive propensity of *Citrullus Colocynthis* fruit for acid corrosion of Aluminium alloy has been analysed at 24 hrs immersion period.

2. EXPERIMENTAL

Preparation of Test Coupons:

Sheet of aluminium alloy achieved locally and of 0.18 cm thickness was mechanically cut into coupons of 2.54 × 1.52 cm^2 size containing a hole of about 0.12 mm diameter near the upper edge for the purpose of hanging in the test solution. Coupons were polished to mirror finish by applying emery paper.

Test solutions & Experimentation :

The electrolytic solutions of H_2SO_4 were prepared by applying bi-distilled water. All chemicals employed were of Analar grade. Ethanolic extraction of *Citrullus Colocynthis* fruits (EE*CC* F) was obtained by refluxing the dried fruits in soxhlet extractor. Each specimen was suspended by the glass hook plunge into a beaker containing 50 ml of the test solution and different concentration of the inhibitor (EE*CC* F). The investigation has been carried out at different elevated temperature (303K to 343K). After fixed intervals of exposure time period, test specimens were washed with running water and dried by hanging the washed specimens in desiccators for sufficient time period [16].

3. RESULTS AND DISCUSSION

Weight Loss studies

Table 1 indicates the value of inhibition efficiency (η%), Fractional surface coverage (θ), Corrosion rate (ρ_{corr}), Adsorption equilibrium constant (K_{ads}) obtained at varying concentration of the inhibitors in 1N H_2SO_4 acid solution for an immersion period of 24 hrs at various elevated temperature in the range 303 – 343 K.

From the mass loss value (ΔM), the inhibition efficiency (η%) was calculated Applying the following equation.

$$\eta\% = [(\Delta M_u - \Delta M_i) / \Delta M_u] \times 100$$

Where ΔM_u is mass loss without inhibitor and ΔM_i is weight loss with inhibitor.

The corrosion rate (ρ_{corr}) in millimetre penetration per year (mmpy) can be determined by following equation [17].

$$\rho_{corr} = (\Delta M \times 87.6) / \text{area} \times \text{time} \times \text{metal density}$$

Where ΔM weight loss expressed in mg, area expressed in cm^2 of metal surface exposed, time expressed in hours of exposure and metal density expressed in gm / cm^3.

Table 1. Gravimetric Parameters for Aluminium alloy in 1N H_2SO_4 in Absence and Presence of Various concentrations of Ethanolic Extract of *Citrullus Colocynthis* fruit extract from Weight Loss Measurements at elevated temperatures for 24 hrs immersion period.

Effective area of specimen 7.72 cm^2 Immersion time 24 hrs

Temperature (K)	EECCF Conc. (%)	Weight Loss ΔM (mg)	Corrosion Rate (ρ_{corr}) (mmpy)	Fractional Surface Coverage (θ)	Adsorption Equilibrium Constant (K_{ads})
303 ± 1	Blank	244.2	42.76	-	-
	0.09	182.6	31.97	0.2522	3.7466
	0.18	152.2	26.65	0.3767	3.3572
	0.27	134.8	23.60	0.4479	3.0044
	0.36	122.2	21.39	0.4995	2.7722
	0.45	98.4	17.23	0.5970	3.2917
313±1	Blank	300.4	52.60	-	-
	0.09	229.4	40.17	0.2363	3.437
	0.18	200.3	35.07	0.3332	2.7761
	0.27	182.5	31.95	0.3924	2.3918
	0.36	152.0	26.62	0.4940	2.7116
	0.45	129.8	22.72	0.5679	2.9204
323±1	Blank	350.6	61.39	-	-
	0.09	276.3	48.38	0.2119	2.9866
	0.18	249.4	43.67	0.2886	2.2533
	0.27	238.2	41.71	0.3205	1.7466
	0.36	203.9	35.70	0.4184	1.9980
	0.45	164.5	28.80	0.5308	2.5137
333 ± 1	Blank	415.8	72.81	-	-
	0.09	340.7	59.66	0.1806	2.4488
	0.18	310.4	54.35	0.2534	1.8855
	0.27	299.9	52.51	0.2787	1.4307
	0.36	278.3	48.73	0.3306	1.3716
	0.45	214.4	37.54	0.4843	2.0868
343± 1	Blank	497.4	87.09	-	-
	0.09	420.6	73.65	0.1544	2.0277
	0.18	397.2	69.55	0.2014	1.4005
	0.27	380.5	66.62	0.2350	1.1374
	0.36	345.4	60.48	0.3055	1.2216
	0.45	305.6	53.51	0.3856	1.3946

Outcomes obtained from the table revealed that the addition of inhibitor to the acid had diminished the corrosion rate (ρ_{corr}). The inhibition efficiency (η%) increased with increase in concentration of inhibitors and decreased with elevation in temperature from 303 K to 343 K in 1N H_2SO_4 acid solution.

Adsorption Isotherm :

Langmuir adsorption isotherm graph was plotted between log (θ / 1- θ) and log C.

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K_{ads} + \log C$$

Where K_{ads} is adsorption equilibrium constant, the K_{ads} value can be calculated from the intercept line on the log (θ / 1 −θ) axis and is related to standard free energy of adsorption.

The values of ΔG^0_{ads} at all studied temperature can be evaluated from the equation as follows [18].

$$\Delta G^0_{ads} = - 2.303\, RT \log (55.5\, K_{ads})$$

Where R = 0.008314 KJ/ mol is the universal gas constant, 55.5 indicate the molar concentration of water in the solution whereas T is the absolute temperature in Kelvin. The values of K_{ads} and ΔG^0_{ads} are shown in table 2 for *Citrullus colocynthis* fruit extract.

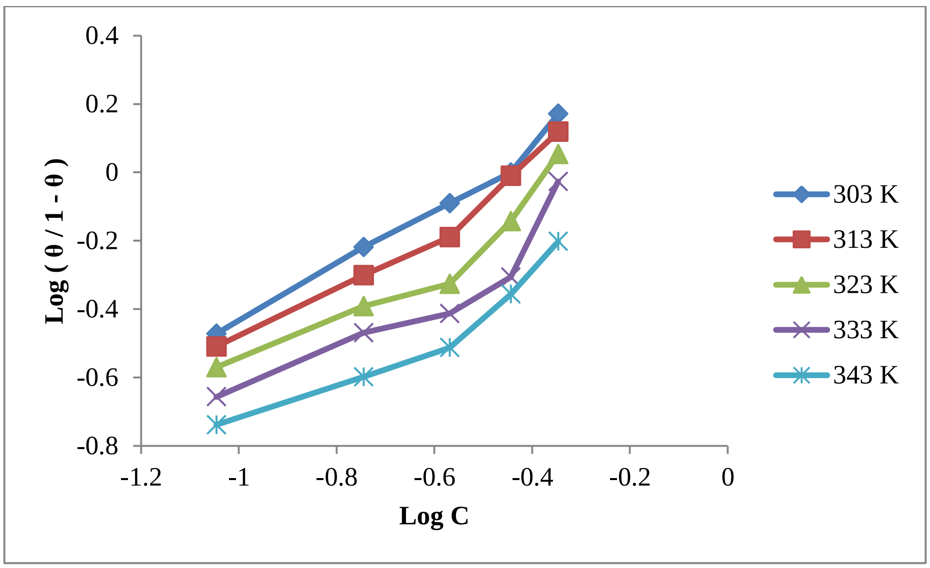

Fig. 1 : Langmuir adsorption isotherm curve for aluminium in 1N H_2SO_4 with fruit extract of *Citrullus colocynthis* at different elevated temperatures at 24 hrs immersion period.

Table 2 : Correlation coefficient (R^2), slopes, Adsorption equilibrium constant (K_{ads}) and Gibbs free energy (ΔG^0_{ads}) from Langmuir adsorption isotherm in 1N H_2SO_4 with Fruit extract of *Citrullus colocynthis* at different temperatures.

Temperature (K)	Slope	R^2	K_{ads}	ΔG^0_{ads} (KJ / mol)
303	0.8664	0.981	2.6510	-12.5760
313	0.8743	0.9657	2.3562	-12.6842
323	0.8229	0.9012	1.7483	-12.2880
333	0.7774	0.8552	1.3035	-11.8555
343	0.7245	0.9175	0.9431	-11.2881

Kinetic / thermodynamic treatment of Weight loss Results : Energy of Activation :

Elevation in temperature has significant influence on the corrosion phenomenon. The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation.

$$\log \rho_{corr.} = \log A - \left(\frac{E_a}{2.303RT}\right)$$

Where ρ_{corr} is the corrosion rate, A is the frequency factor, R is the universal molar gas constant, E_a is the apparent activation of energy and T is the absolute temperature in kelvin.

Fig.2 for *Citrullus colocynthis* indicates the linear graph for plot of log $\rho_{corr.}$ versus 1 / T. Activation energy values E_a were estimated from slopes of log $\rho_{corr.}$ versus 1 / T . The slope of Arrhenius curve is equal to $-E_a / 2.303$ R.

The positive sign for both E_a and ΔH_{act} indicate the endothermic nature of corrosion process / phenomenon.

Other kinetic parameters of the corrosion reaction, namely, entropy ΔS and enthalpy ΔH of activation transition state were obtained from the transition state equation [19].

$$\rho_{corr} = \left(\frac{RT}{Nh}\right) e^{\left(\frac{\Delta S_{act}}{R}\right)} e^{\left(\frac{-\Delta H_{act}}{RT}\right)}$$

$$\log\left(\frac{\rho_{corr}}{T}\right) = \left[\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_{act}}{2.303R}\right)\right] - \left(\frac{\Delta H_{act}}{2.303RT}\right)$$

Where $\rho_{corr.}$ is the corrosion rate, h is the plank's constant, N is the Avogadro' s number, R is the universal gas constant and T is the absolute temperature.

A plot of log (ρ_{corr} / T) versus 1 / T give a straight line Fig.3 were obtained with the slope of (- ΔH_{act} / 2.303 R) and intercept of [log (R / N h) + (ΔS_{act} / 2.303 R)] from which the values of ΔH_{act} and ΔS_{act} respectively, were evaluated from the slope and intercept respectively from the linear plot . The estimated values of E_a, ΔH_{act} and ΔS_{act} are depicted in table 3 for aluminium in 1N H_2SO_4.

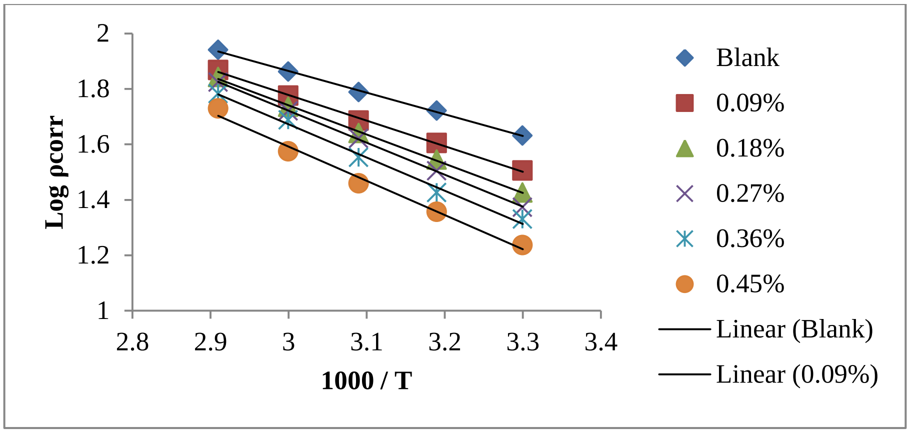

Fig. 2 : Arrhenius plots for aluminium corrosion in 1N H_2SO_4 with fruit extract of *Citrullus colocynthis* at 24 hrs immersion period.

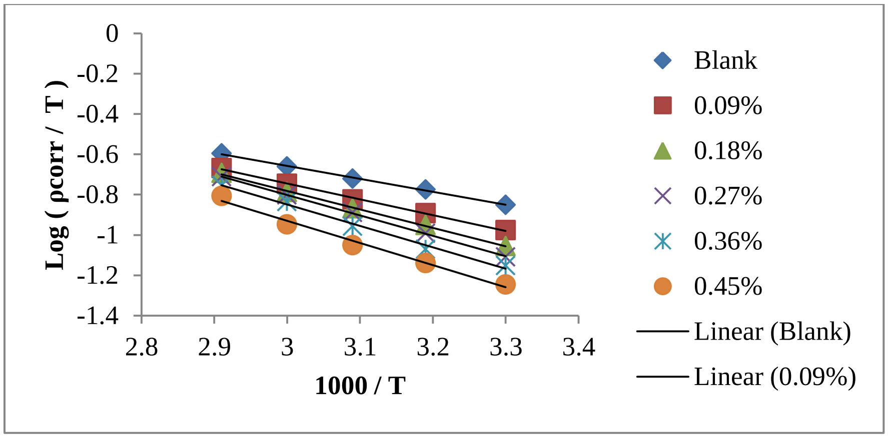

Fig. 3 : Transition state plots for aluminium corrosion in 1N H_2SO_4 with fruit extract of *Citrullus colocynthis extract* at 24 hrs immersion period.

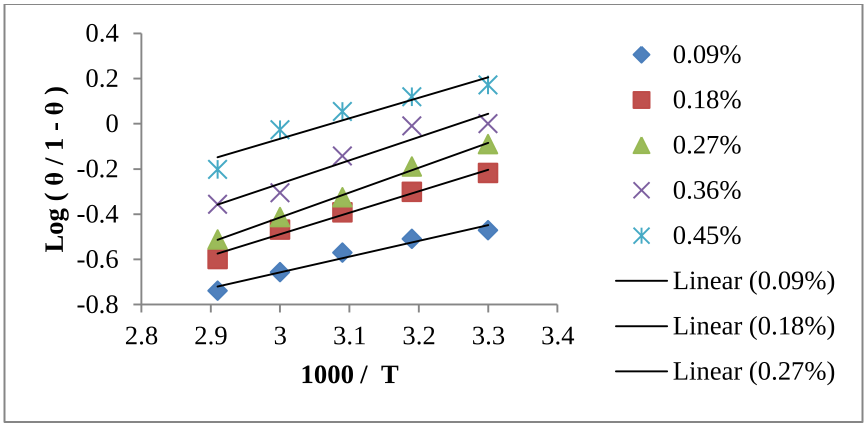

Fig. 4 : log (θ / 1 – θ) vs 1 / T for different concentration of *Citrullus Colocynthis* fruit extract in 1N H_2SO_4 at 24 hrs immersion period.

Table 3 : Kinetic – thermodynamic parameters for aluminium corrosion in 1N H_2SO_4 without and with fruit extract of *Citrullus Colocynthis* at various concentrations at immersion time 24 hrs.

Concentration of Inhibitor (%)	Activation Energy E_a (kJ / mol)	Enthalpy ΔH_{act} (kJ / mol)	Entropy ΔS_{act} (J / mol / K)	Heat of adsorption Q_{ads} (kJ / mol)
Blank	14.96	12.31	-173.19	-
0.09	17.66	15.01	-166.77	-13.31
0.18	20.18	17.54	-159.89	-18.22
0.27	22.06	19.43	-154.61	-21.05
0.36	22.93	20.30	-152.89	-19.72
0.45	23.64	21.01	-152.33	-17.39

Thermodynamic Parameters : Thermodynamic adsorption parameters such as the enthalpy of adsorption (ΔH_{ads}) and the entropy of adsorption (ΔS_{ads}) were also determined from the experimental data. ΔH^0_{ads} and ΔS^0_{ads} are obtained using the following equation

$$\Delta G^0_{ads} = \Delta H^0_{ads} - T\,\Delta S^0_{ads}$$

The values of ΔS^0_{ads} was obtained from the slope and the intercept leads to ΔH^0_{ads} (table 4). The entropy (ΔS^0_{ads}) values are positive in almost all cases confirming that the corrosion process is entropically favourable.

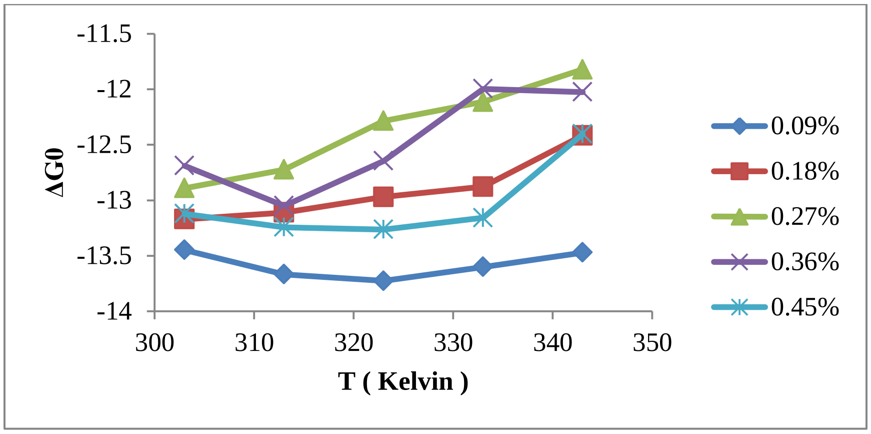

Fig. 5 : Plot of ΔG^0 vs T (K) for various concentration of *Citrullus Colocynthis* fruit extract in 1N H_2SO_4 at 24 hrs immersion period.

Table 4 : Thermodynamic parameters for aluminium corrosion in 1N H_2SO_4 in the absence and presence of various concentrations of *Citrullus Colocynthis* fruit extract of at elevated temperatures (303 – 343 K) at immersion time 24 hrs.

Inhibitor Concentration (%)	ΔG^0_{ads}					ΔH^0_{ads}	ΔS^0_{ads}
	303 K	313 K	323 K	333 K	343 K		
Blank	-	-	-	-	-	-	-
0.09	-13.44	-13.66	-13.72	-13.60	-13.47	-13.64	-0.0002
0.18	-13.17	-13.11	-12.96	-12.87	-12.41	-18.53	-0.0174
0.27	-12.89	-12.72	-12.28	-12.11	-11.82	-21.23	-0.0275
0.36	-12.68	-13.04	-12.64	-11.99	-12.02	-20.17	-0.0238
0.45	-13.12	-13.24	-13.26	-13.15	-12.40	-17.94	-0.0152

CONCLUSIONS

Following conclusions may be drawn on the basis of the results obtained from study of the effect of elevation in temperature on the protective propensity of *Citrullus Colocynthis* fruit extract on acid corrosion of aluminium alloy in 1N H_2SO_4.

- *Citrullus Colocynthis* fruit can be good inhibitor to impede acid corrosion of aluminium in 1N H_2SO_4 at 303 K with maximum inhibition efficiency of 59.70 % in 0.45% concentration.
- Elevation in corrosion rate at high temperature but with the additive, a reasonable decrease in corrosion rate was observed.
- Activation energy E_{act} in aggressive medium alone (blank) was observed much lower as compared to that in inhibited test solutions. E_{act} of EE*CC*F was found in the range of 14.96 to 23.64 KJ / mol.
- The adsorption of the extract on the mild steel was spontaneous and obeyed Langmuir adsorption isotherm at elevated temperatures.
- Entropy of adsorption decreases with increase in EE*CC*F indicates association of inhibitor molecules.
- Overall, it can be concluded that *Citrullus Colocynthis* fruit extract can be used as green inhibitor to replace toxic chemicals used to impede aluminium alloy corrosion in 1N H_2SO_4 at elevated temperature up to 343 K.

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