

Review Article

Adsorption and Inhibitive Properties of Peel extract of *Cucurbita maxima* as Green Inhibitor for Aluminium in 1N HCl

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Abstract

The corrosion inhibition of aluminium in 1N HCl solution by the peel of *Cucurbita maxima* (PCM) extract was investigated by weight loss measurement. It was found that the plant extract retarded the acid induced corrosion of aluminium. Inhibition efficiency (IE) increased with increasing concentration of the extract and decreased with increasing temperature. The maximum IE of 99% was obtained for 1.5% v/v PCM at 303K for 1h. The adsorption process follows Langmuir adsorption isotherm. Activation parameters such as activation energy (E_a), activation enthalpy (ΔH^*), and activation entropy (ΔS^*) were evaluated from the effect of temperature on the corrosion and inhibition processes. The ΔG_{ads} values suggested that the inhibitor was adsorbed on the aluminium surface mainly by physisorption.

Keywords: *Cucurbita maxima*, Langmuir, Adsorption, Aluminium, physisorption.

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Introduction

Aluminium is a metal with a high electronegative potential (-1.67 v). It is also highly resistant to most acidic and neutral solution due to the formation of a protective oxide films on its surface. The film is responsible for the corrosion resistance of aluminium in most environments [1]. However when aluminium is exposed to high concentrations of acids or bases the passive film is dissolved, under these conditions corrosion inhibitors should be used. Aluminium and its alloys have proved to be strategically important materials and have extensive use in many industries. They are used in the automotive, aviation and aero-space industries, in the making of household appliances, in ship building and military hardware [2-4]. Corrosion control of aluminium by organic inhibitors of plant origin, are viable and highly beneficial since they are essentially non-toxic, environmentally benign, readily available, renewable and inexpensive [5-11]. Extracts of some plants such as *Cocus nucifera* [12], *Delonix regia* [13], *Opuntia* [14], *Vernonia amydalina* [15] and *Sansevieria trifasciata* [16] have been reported to inhibit the rate of acid corrosion of Al. Their inhibitive effect has been attributed to the adsorption of the phytochemicals on the Al surface which leads to slowing down of the electrochemical processes on the metal surface. In this study, the inhibitory action of acid extract of peel of *Cucurbita maxima* (PCM) on the corrosion of aluminium in 1N HCl solution has been investigated at five different temperatures (303K, 313K, 323K, 333K & 343 K) using weight loss method.

Materials and Methods**Preparation of Specimens**

The industrially available Aluminium of grade 8011 was purchased at Coimbatore Metal Mart, Coimbatore -18, Aluminium sample was tested for purity at SiTarc Coimbatore 18. The aluminium sheet was mechanically press cut into (5 x 1 cm) rectangular pieces. They are polished using (400 and 600) grades of emery sheet to mirror finish, degreased and finally washed with distilled water and then dried. Thereafter, they are kept in desiccator overnight and then weighed using a digital balance.

Preparation of PCM Extract

The peel of *Cucurbita maxima* was collected and shade dried and ground well into powder. 15 g of it was refluxed with 300 ml of 1N HCl for 3 hours. It was kept overnight and filtered. From this bulk the inhibitor test solutions of 0.01%, 0.05%, 0.1%, 0.5 %, 1% 1.5%, 2%, 2.5%, 3% v/v concentrations were prepared. 1N HCl was used as corrodent.

Weight Loss Method

The weight loss experiments were carried out on aluminium specimens in temperature range of 303K – 343 K to investigate the effect of temperature on corrosion using the different concentrations of PCM in 1N HCl for immersion period of 1 hour. The corrosion rate (CR) and inhibition efficiency (IE) were calculated from the following formulas [17].

Corrosion Rate

This is expressed in millimeter per year (mm/y)

$$\text{Corrosion Rate (CR) (mm/y)} = \frac{87.6 \times W}{DA t}$$

Where W = Weight loss (mg), D = Density of the coupon (2.8 g/cm³), A = Area of coupon (cm²), t = Time of exposure (hours)

Inhibition Efficiency (IE %)

The percentage inhibition efficiency (IE %) was calculated from the following equation.

$$\text{IE \%} = \frac{(\text{CR}_{\text{Blank}} - \text{CR}_{\text{Inhibitor}}) \times 100}{(\text{CR}_{\text{Blank}})}$$

CR_{Blank} = Corrosion rate in the absence of inhibitor.

CR_{Inhibitor} = Corrosion rate in the presence of inhibitor.

Surface Coverage (θ)

The surface coverage was calculated from the following equation.

$$\text{Surface coverage } (\theta) = \frac{W_2 - W_1}{W_1}$$

Where, W₁ = Corrosion rate in the absence of inhibitor.

W₂ = Corrosion rate in the presence of inhibitor.

Results and Discussion**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 over potential increases [18]. In order to assess the effect of temperature on the corrosion and corrosion inhibition process, weight loss experiments were carried out in the temperature range 303K to 343 K in 1N HCl in the absence and presence of different concentrations

of PCM extract. Arrhenius-type dependence is observed between corrosion rate and temperature often expressed as follows [19]

$$CR = Ae^{-E_a/RT}$$

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. It is clear that, the corrosion process is inhibited via increasing the activation energy of the reaction.

The increase in activation energy is achieved via formation of an adsorbed film on the metal surface leading to retarding the energy and mass transfer. However, increasing temperature retards this effect by enhancing the desorption process and thus the inhibition efficiency of the PCM is decreased. The CR, IE and θ values are listed in Tables 1 and 2. The plot of CR versus temperature with different concentrations of PCM is shown in Figure 1. The plot of IE versus temperature with different concentrations of PCM is shown in Figure 2. Inhibition efficiency increases with concentration but decreases with increase in temperature. Maximum inhibition efficiency of 99% obtained at 1.5 % v/v PCM concentration at 303K.

Table 1 CR of Aluminium and IE of PCM in 1N HCl at Different Temperatures.

S.No	Conc.of PCM %v/v	303K		313K		323K		333K		343K	
		CR mm/y	IE %	CR mm/y	IE %	CR mm/y	IE %	CR mm/y	IE %	CR mm/y	IE %
1	Blank	1325	-	3211	-	3311	-	2183	-	2545	-
2	0.01	256	80	2307	28	2698	18	2146	3	2158	15
3	0.05	61	95	2024	36	2476	25	2100	3	2151	16
4	0.1	60	95	2006	37	2249	32	2094	4	2145	16
5	0.5	15	98	1989	38	2058	34	2023	7	2122	17
6	1	13	98	1778	44	1961	40	2005	8	2098	18
7	1.5	9	99	1200	62	1907	42	1953	10	2092	18
8	2	9	99	851	73	1864	43	1887	13	2085	18
9	2.5	8	99	835	73	1718	46	1835	15	2011	21
10	3	6	99	773	75	1631	50	1631	25	1762	31

Table 2. Calculated Surface Coverage Values at Different Temperatures.

S.No	Conc.of PCM %v/v	Surface coverage (θ)				
		303K	313K	323K	333K	343K
1	Blank	-	-	-	-	-
2	0.01	0.8064	0.2814	0.1849	0.169	0.1521
3	0.05	0.9533	0.3695	0.2534	0.26	0.1551
4	0.1	0.9543	0.3751	0.3205	0.408	0.1572
5	0.5	0.9879	0.3803	0.3481	0.733	0.1663
6	1	0.9895	0.4462	0.4077	0.813	0.1755
7	1.5	0.9926	0.6261	0.421	0.1052	0.178
8	2	0.9931	0.7347	0.4369	0.1354	0.1807
9	2.5	0.9937	0.7397	0.4619	0.1593	0.2099
10	3	0.9947	0.7592	0.5072	0.2529	0.3077

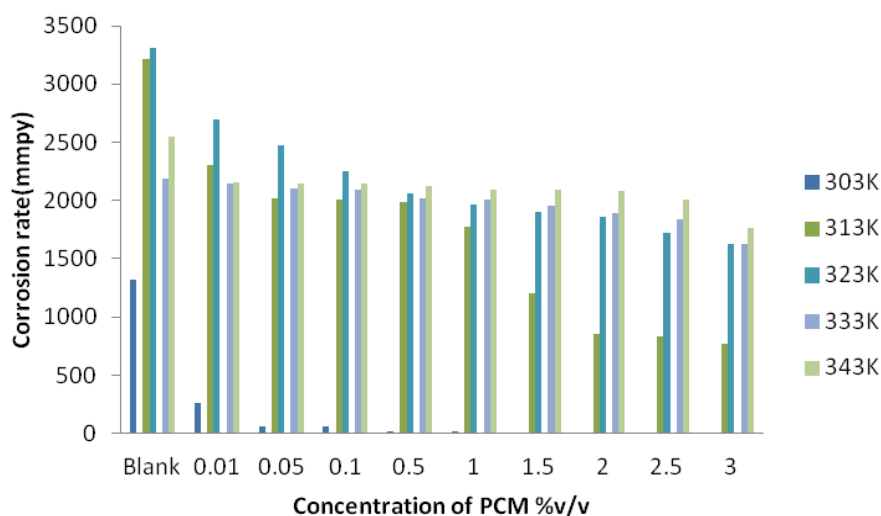


Figure 1 Corrosion Rate of Aluminium at different temperatures

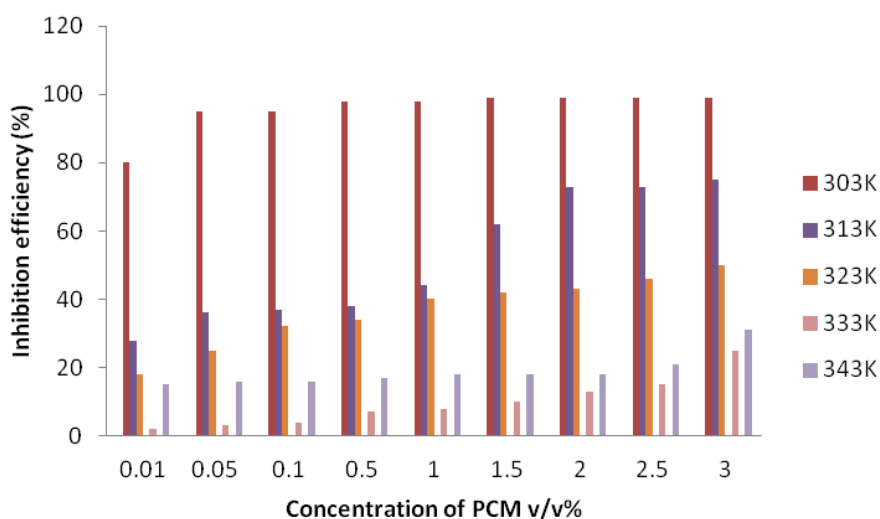


Figure 2 Inhibition Efficiency of PCM at different temperatures

Adsorption isotherm

Inhibition effects are based on the adsorption of molecules onto the metal surface to form an impermeable protective film and shielding it from the corrosive media. On the other hand, the adsorbed molecules can combine with the oxide layer on the metal (rust deposited) and react chemically to produce a more protective surface network and change the structure. The adsorption mechanism of organic compounds performs either directly, on the basis of donor-acceptor interactions between relatively loosely bound electrons such as in anions and organic molecules and/or the heterocyclic compound which has lone pair electrons or the π -electrons with the vacant d-orbital of iron atoms of metal [20]. Some parameters of organic molecules such as molecule size, number of functional groups, polarity that contributed to the formation of the strongest bonding or rate of adsorptions of inhibitor compounds onto the surface could affect the adsorption mechanism or inhibition action. 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. Langmuir adsorption isotherm is given by the following equation

$$C/\theta = 1/K + C$$

where K is the equilibrium constant for adsorption process which reflects the extent of interaction between the inhibitor and the metal surface and C is the concentration of the inhibitor. ΔG_{ads} was calculated using the following equation[21]

$$\Delta G_{\text{ads}} = -RT \ln(55.5K_{\text{ads}})$$

where R is molar gas constant (8.314 J/K), T is temperature in Kelvin and value 55.5 is the molar concentration of water in solution.

It is evident that the inhibition efficiency and surface coverage increased with increasing inhibitor concentration and decreased with increasing temperature, from 303-343 K. This is suggestive of physical adsorption (physisorption) mechanism. Figure 3 shows that the inhibition efficiency ranges from 80% to 99% at 303K whereas at high temperature (343K) it is much lower ranging from 15% to 30% for the different concentration of the inhibitor. This confirms physical adsorption for the inhibition process. The plot of C/θ against C yields straight lines shown in Figure 4. It is evident to note that the linear correlation value is almost equal to 1 indicates that the adsorption of PCM on aluminium surface obeys Langmuir adsorption isotherm. The plot of $\log CR$ versus $1/T$ yields straight lines as shown in Figure 5 indicates the Arrhenius adsorption isotherm.

The high surface coverage data observed at high inhibitor concentration is due to very strong interactions between the adsorbed species. The surface coverage data also implies that the adsorption of *Cucurbita maxima* at the aluminium interface may be due to electrostatic force between the atoms on the metal surface and the adsorbates (inhibitor molecules).

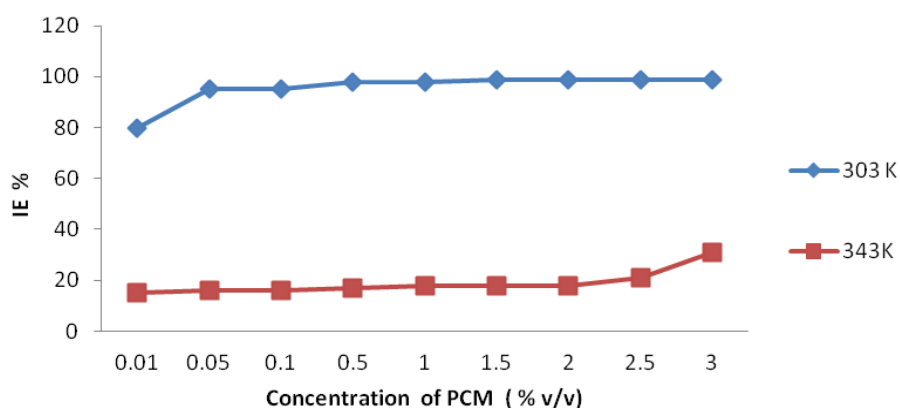


Figure 3 Concentration of Inhibitor versus Inhibition Efficiency at lower and higher temperature range

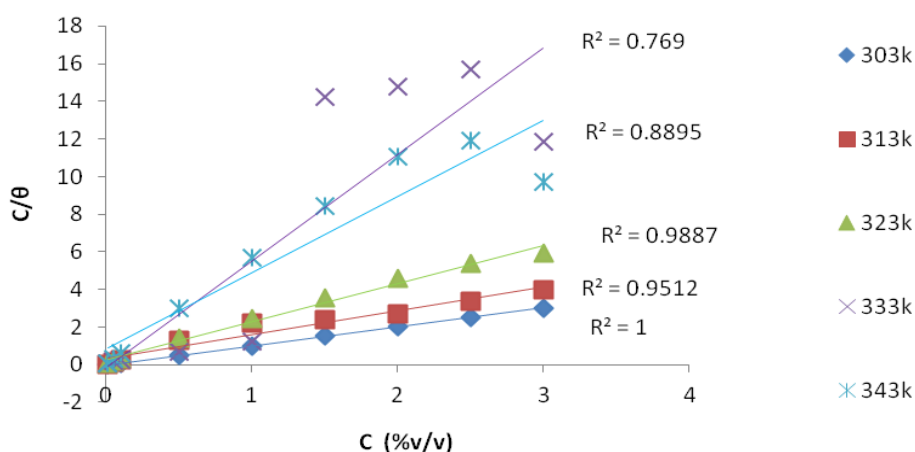


Figure 4 Langmuir adsorption isotherm plot for aluminium corrosion in 1N HCl

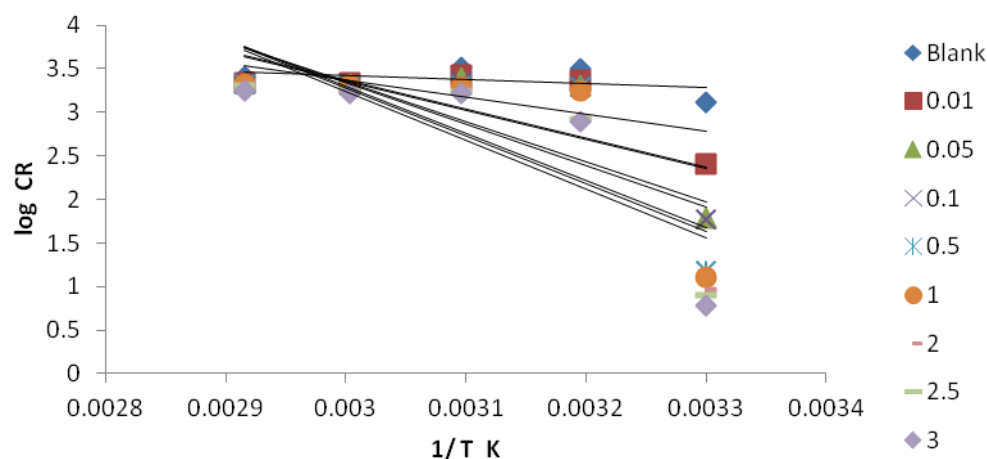


Figure 5 Arrhenius plot of Aluminium in 1N HCl solution with different concentrations of PCM

The value of activation energy for blank (8.46kJ/mol) is lower than in the presence of PCM inhibitor (107.39kJ/mol). This increase of apparent activation energy for aluminium dissolution with inhibitor may be interpreted as physical adsorption mechanism. The positive sign of the ΔH^* reflects the endothermic nature of the aluminium dissolution process [22] in the presence of the PCM extract. The calculated values of activation parameters E_a , ΔH^* and ΔS^* and the thermodynamic parameter ΔG_{ads} are given in Tables 3 and 4 respectively.

Table 3 Calculated Thermodynamic parameter ΔG_{ads}

S.No	Concentration of PCM (%v/v)	$-\Delta G_{ads}$ (KJ/mol)				
		303K	313K	323K	333K	343K
1	BLANK	-	-	-	-	-
2	0.01	25.29	19.97	19.14	19.37	18.51
3	0.05	25.24	16.83	15.90	16.42	14.25
4	0.1	23.55	15.09	14.92	16.37	12.43
5	0.5	22.93	10.96	10.93	15.74	8.29
6	1	21.54	9.86	9.75	15.09	6.60
7	1.5	21.41	10.71	8.81	3.97	5.56
8	2	20.86	11.27	8.21	3.97	4.83
9	2.5	20.53	10.76	7.88	3.88	4.73
10	3	20.51	10.55	7.88	4.98	5.63

Table 4 Calculated Activation parameters.

S.No	Concentration of PCM (%v/v)	E_a kJ/mol	ΔH^* J/mol	$-\Delta S^*$ J/mol
1	Blank	8.46	-	-
2	0.01	37.49	268	5558
3	0.05	63.84	280	4620
4	0.1	64.09	279	4701
5	0.5	88.32	292	3510
6	1	91.51	292	3529
7	1.5	101.05	292	3595
8	2	103.54	291	3848
9	2.5	104.90	291	3790
10	3	107.39	294	3597

Conclusions

- The peel of *Cucurbita maxima* (PCM) acts as green inhibitor for corrosion of aluminium in 1N HCl solution. The IE increases with increasing extract concentration.
- The results of weight loss measurement for different concentrations of inhibitor at higher temperature shows maximum inhibition efficiency of 99% at 1.5% PCM at 303K for 1h.
- The inhibition action is due to the adsorption of the extract compounds on aluminium surface. The adsorption process is physical in nature and follows Langmuir adsorption isotherm.
- The presence of PCM extract increases the activation energy of the corrosion reaction.
- The negative values of ΔG_{ads} reveal the spontaneity of the adsorption process and the values range from -5 kJ/mol to -25kJ/mol indicating the physical adsorption.

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