Corrosion Inhibition of Aluminium in Acid Media By *Citrullus Colocynthis* Extract

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Abstract: Inhibition of corrosion of aluminium in acid solution by methanol extract of *Citrullus colocynthis* plant has been studied using mass loss and thermometric measurements. It has been found that the plant extract act as a good corrosion inhibitor for aluminium in all concentrations of sulphuric and hydrochloric acid solution. The inhibition action depends on the concentration of acid and inhibitor. Results for mass loss and thermometric measurement indicate that inhibition efficiency increase with increasing inhibitor concentration. The inhibition action of the plant extract is discussed in view of Langmuir adsorption isotherm. It has been observed that the adsorption of the extract on aluminium surface is a spontaneous process. The plant extract provides a good protection to aluminium against corrosion.

Keywords: Metal, Corrosion inhibitor, Surface coverage and Langmuir adsorption isotherm.

Introduction

Corrosion is a natural phenomenon, which can be considered either chemical or electrochemical in nature, degrades the metallic properties of metal and alloys make them unfit for specific role. Aluminium is a soft, durable, lightweight, malleable metal with appearance ranging from silvery to dull gray, depending on the surface roughness. Aluminium is nonmagnetic and nonsparking. Aluminium and its alloy recommended for building purpose and for various internal outfits, at various industries and highly polluted places. Aluminium is remarkable for the metal's low density and for its ability to resist corrosion to some extent due to the phenomenon of passivation. But its corrosion takes place in aqueous acidic conditions.

The corrosion of aluminium and its alloy in acid solutions have extensively been studied¹⁻³. Some chemicals as corrosion inhibitor are currently used in industry to prevent or to reduce the corrosion rates of metals in acid media. Due to toxic nature and high cost of these chemicals it is necessary to develop environmentally acceptable and less expensive inhibitors. Some natural products have been evaluated as potential corrosion inhibitors for different metals^{4,5}. Natural product of plant origin contain different organic compounds (*viz-* Alkaloids, Steroids, Amino acids, Tannins, Flavanoids *etc.*) and most are known to have inhibitive action⁶⁻⁷.

The present communication describes the influence of various concentration of the extract of *Citrullus colocynthis* plant on corrosion behavior of aluminium in acid media by mass loss and thermometric measurements.

Chemical constituents of plant

The plant has very high medicinal value⁸. The plant contains three antitumor ingredients: cucurbitacin B, cucurbitacin E and the D-glucoside of *beta*- sitosterol. The pulp contains colocynthin, extractive, a fixed oil, a resinous substance insoluble in ether, gum, pectin, water and calcium and magnesium phosphates. Seeds contain the phyto sterolin, two hydrocarbons, an alkaloid, glycoside and tannin⁹. Roots contain hentriacontane and saponin.

Experimental

The *Citrullus colocynthis* extract was obtained by drying the plant part, then finely powered and extracted with boiling in methanol. The solvent was distilled off and the residue was treated with activated charcoal to remove gangue and pure extract of *Citrullus colocynthis* was used as probable corrosion inhibitor for aluminium metal. Inhibition efficiency was calculated by two methods.

Mass loss method¹⁰

Rectangular size specimens of aluminium metal foils of dimension 2.5 × 1.5 × 0.03 cm containing a small hole of about 3 mm diameter near the upper edge were employed for the experiment. Specimens were cleaned by buffing to produce a mirror finish with the help of emery paper and then weighed. Each specimen was suspended by a V-shaped glass hook in a beaker containing 50 mL of test solution (acidic) at room temperature and left exposed to air. The acidic solution was prepared by using doubly distilled water and evaporation losses were made up with doubly distilled water. After the experiment, specimens were took out of the beaker, cleaned with benzene and weighed again. A set of duplicate experiments were performed in each case and mean values of the mass loss were calculated. All chemicals used were of analytical reagent quality.

The degree of surface coverage (θ) can be calculated as:

$$\theta = \Delta Mu - \Delta Mi / \Delta Mu$$

Where, ΔMu and ΔMi are the mass loss of the metal in uninhibited and inhibited acid respectively. The corrosion rate in *mmpy* (millimiles per year) can be obtained by the following equation:

$$\text{Corrosion rate, mmpy} = \frac{\text{Mass loss} \times 87.6}{\text{Area} \times \text{Time} \times \text{Metal density}}$$

Where mass loss is expressed in mg, area is expressed in cm² of metal surface exposed, time is expressed in hours of exposure, and metal density is expressed in gms/cm³ and 87.6 is a conversion factor. The percentage inhibition efficiency ($\eta\%$) was calculated as :

$$(\eta \%) = 100 (\Delta Mu - \Delta Mi / \Delta Mu)$$

Thermometric method¹¹

Inhibition efficiencies were also determined using a thermometric technique. This involved the immersion of single specimen measuring 2.5 x 1.5 x 0.03 cm in a reaction chamber containing 50 mL of test solution. Temperature changes were measured at interval of one minute using a thermometer with a precision of 0.01 K. The temperature first increased slowly, then rapidly and attained a maximum value and then start decreasing. The highest temperature was recorded. Percentage inhibition efficiency was calculated as:

$$(\eta \%) = 100 (RN_{free} - RN_i) / RN_{free}$$

Where RN_i and RN_{free} are the reaction number in the presence and absence of inhibitors respectively and RN (K/min) is defined as:

$$RN = (T_m - T_o) / t$$

Where T_m and t_o are the maximum and initial temperature respectively and t is the time required to reach the maximum temperature.

Results and Discussion

Values of mass loss, surface coverage, percentage inhibition efficiency ($\eta\%$) and corrosion rate at different concentrations of acid and inhibitor are given in Table 1 and 2. It is observed that the inhibition efficiency increases with increasing acid and inhibitor concentration because the inhibitor ionizes more easily under more acidic solution and is more easily adsorbed on the metal surface, thus increasing the inhibition efficiency. All the inhibitors reduce the corrosion rate to a significant extent. The maximum efficiencies are obtained at 1 N hydrochloric acid concentration. The inhibitor shows efficiencies in the range from 71.84% to a maximum 87.29% for methanol extract (Table 2).

Table 1. Mass loss, surface coverage, inhibition efficiency and corrosion rate for aluminium in 0.5 N and 1.0 N H_2SO_4 solution with methanolic extract of *Citrullus colocynthis* for 24 h at 298 ± 0.1 K

Inhibitor concentration	Mass loss	Surface coverage θ	Inhibition efficiency	Corrosion rate	Mass loss	Surface coverage θ	Inhibition efficiency	Corrosion rate
Uninhibited	120.70	-	-	21.76	145.5	-	-	26.23
Leaves extract		0.5 N H_2SO_4				1.0 N H_2SO_4		
0.12	55.10	0.5435	54.35	9.93	49.96	0.6566	65.66	9.01
0.24	51.25	0.5754	57.54	9.24	42.09	0.7107	71.07	7.59
0.36	47.46	0.6068	60.68	8.55	39.74	0.7269	72.69	7.16
0.48	43.22	0.6419	64.19	7.79	32.30	0.7780	77.80	5.82
0.60	37.25	0.6914	69.14	6.71	29.90	0.7945	79.45	5.39
Seeds extract		0.5 N H_2SO_4				1.0 N H_2SO_4		
0.12	54.41	0.5492	54.92	9.81	52.03	0.6424	64.24	9.38
0.24	50.85	0.5787	57.87	9.17	44.10	0.6969	69.69	7.95
0.36	46.95	0.6110	61.10	8.46	39.59	0.7279	72.79	7.14
0.48	38.33	0.6824	68.24	6.91	34.57	0.7624	76.24	6.23
0.60	31.38	0.7400	74.35	5.66	27.98	0.8077	80.77	5.04

Table 2. Mass loss, surface coverage, inhibition efficiency and corrosion rate for aluminium in 0.5 N and 1.0N HCl solution with methanolic extract of *Citrullus colocynthis* for 24 h at 298±0.1K

Inhibitor concentration	Mass loss	Surface coverage θ	Inhibition efficiency	Corrosion rate	Mass loss	Surface coverage θ	Inhibition efficiency	Corrosion rate
Uninhibited	177.7	-	-	32.03	233.7	-	-	42.12
Leaves extract		0.5N HCl				1.0N HCl		
0.12	49.66	0.5886	58.86	8.95	65.81	0.7184	71.84	11.86
0.24	46.86	0.6118	61.18	8.45	60.72	0.7402	74.02	10.94
0.36	44.31	0.6329	63.29	7.99	53.00	0.7732	77.32	9.55
0.48	36.49	0.6977	69.77	6.58	35.83	0.8467	84.67	6.46
0.60	26.34	0.7818	78.18	4.75	29.70	0.8729	87.29	5.35
Seeds extract		0.5N HCl				1.0N HCl		
0.12	47.52	0.6063	60.63	8.57	77.47	0.6685	66.85	13.96
0.24	44.31	0.6329	63.29	7.99	73.38	0.6860	68.60	13.23
0.36	36.22	0.6999	69.99	6.53	70.62	0.6978	69.78	12.73
0.48	33.61	0.7215	72.15	6.06	53.00	0.7732	77.32	9.55
0.60	30.27	0.7492	74.92	5.46	38.30	0.8361	83.61	6.90

Inhibition efficiency values were also determined by using thermometric techniques. Temperature change for aluminium in 3 N, 4 N and 5 N hydrochloric acid and sulphuric acid solution were recorded at various inhibitor concentrations. However no significant temperature changes were recorded at an acid concentration of 1 N and 2 N hydrochloric acid solution. Therefore, use of the thermometric method was restricted to 3 N-5 N hydrochloric acid and sulphuric acid solution. The results summarized in Table 3 and 4 are in broad agreement with those obtained from mass loss measurement. The variation of reaction number with inhibitor concentrations, presented graphically shows essentially linear behavior with the negative slop indicating that the reaction number decreases with increasing inhibitor concentration.

Table 3. Reaction number (RN) and percentage inhibition efficiency ($\eta\%$) for aluminium in H_2SO_4 solution with given inhibitor extract at 298 ±0.1K

Inhibitor concentration	Reaction Number, K min^{-1}	Inhibition efficiency, $\eta\%$	Reaction Number, K min^{-1}	Inhibition efficiency, $\eta\%$	Reaction number, K min^{-1}	Inhibition efficiency, $\eta\%$
Uninhibited	0.0967	-	0.2546	-	1.1082	-
Leaves extract	3N H_2SO_4		4N H_2SO_4		5N H_2SO_4	
0.12	0.0288	66.88	0.7289	63.28	1.3278	58.90
0.24	0.0276	68.29	0.6573	66.89	1.1856	63.30
0.36	0.0245	71.76	0.6067	69.44	1.1067	65.74
0.48	0.0209	75.96	0.5478	72.40	1.0189	68.46
0.60	0.0187	78.52	0.4589	76.88	0.9845	69.52
Seeds extract	3N H_2SO_4		4N H_2SO_4		5N H_2SO_4	
0.12	0.0319	63.30	0.8190	58.74	1.5023	53.49
0.24	0.0288	66.90	0.7678	61.32	1.4089	56.39
0.36	0.0257	70.46	0.7183	63.81	1.329	58.86
0.48	0.0221	74.55	0.6389	67.81	1.2456	61.44
0.60	0.0209	75.98	0.5689	71.34	1.0111	68.70

Table 4. Reaction number (RN) and inhibition efficiency ($\eta\%$) for aluminium in HCl solution with given inhibitor extract at $298 \pm 0.1\text{K}$

Inhibitor concentration	Reaction number, K min^{-1}	Inhibition efficiency, $\eta\%$	Reaction number, K min^{-1}	Inhibition efficiency, $\eta\%$	Reaction Number, K min^{-1}	Inhibition efficiency, $\eta\%$
Uninhibited	2.2128	-	5.8445	-	8.0219	-
Leaves extract	3 N HCl		4 N HCl		5 N HCl	
0.12	0.0327	66.16	0.0976	61.68	0.5122	53.78
0.24	0.0238	75.34	0.0696	72.65	0.4447	59.87
0.36	0.0202	79.11	0.0654	74.32	0.3888	64.92
0.48	0.0144	85.13	0.0504	80.22	0.3398	69.34
0.60	0.0097	90.01	0.0368	85.54	0.2846	74.32
Seeds extract	3 N HCl		4 N HCl		5 N HCl	
0.12	0.0334	65.43	0.0990	61.12	0.5146	53.56
0.24	0.0268	72.31	0.0795	68.78	0.4591	58.57
0.36	0.0193	80.01	0.0619	75.67	0.4008	63.83
0.48	0.0139	85.64	0.0486	80.90	0.3301	70.21
0.60	0.0105	89.11	0.0365	85.65	0.2802	74.72

Adsorption plays an important role in the inhibition of metallic corrosion by inhibitors. Many investigators have used the Langmuir adsorption isotherm to study inhibitors characteristics¹² assuming that the inhibitors adsorbed on the metal surface decrease the surface area available for corrosion. Langmuir adsorption isotherm should give a straight line of unit gradient for the plot of $\log [\theta / 1 - \theta]$ versus $\log C$.

$$\log [\theta / 1 - \theta] = \log A + \log C - (\theta / 2.3RT)$$

Where, θ is degree of surface coverage, A is a temperature independent constant and C is a concentration of the inhibitor. The corresponding plot (Figures 1-4) is linear but the gradients are not equal to unity as would be expected for the Langmuir adsorption isotherm equation. This deviation from the unity may be explained on the basis of the interaction among the adsorbed species on the metal surface.

Figure 1. Langmuir adsorption isotherm of leaves extract for aluminium in $0.5\text{N H}_2\text{SO}_4$ with inhibitor concentration **Figure 2.** Langmuir adsorption isotherm of leaves extract for aluminium in $1.0\text{N H}_2\text{SO}_4$ with inhibitor concentration

Figure 3. Langmuir adsorption isotherm of leaves extract for aluminium in 0.5N HCl with inhibitor concentration

Figure 4. Langmuir adsorption isotherm of leaves extract for aluminium in 1N HCl with inhibitor concentration.

Conclusion

The study of the extract of plant *Citrullus colocynthis* in different acid concentration solutions have proved them to be effective inhibitors of the corrosion of aluminium giving up to 87.29% inhibition efficiency. Its adsorption on aluminium obeyed Langmuir adsorption isotherm. The results shows that the plant is the rich sources of ingredients which have very high inhibition efficiency have become important as an environmentally acceptable, readily available, less toxic and renewable source for wide range of inhibitors.

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