RESEARCH ARTICLE

Green Corrosion Inhibitor by Ethanolic Extract of *Lantana camara* for corrosion of aluminium in acidic media

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Abstract:

The corrosion inhibition of aluminium in sulphuric acid solution in the presence of different plant parts viz. leaves, stem bark and fruit was studied using weight loss method and thermometric method. The ethanolic extracts of *Lanatana camara* were found to inhibit corrosion. The inhibition efficiency was found to increase with the increase in inhibitor concentration. The inhibition was attributed to the adsorption of the plant part on the surface of aluminium metal. The green corrosion inhibitors are cheap, easily available and biodegradable.

Keywords: Corrosion inhibition, Aluminium, Adsorption, *Lanatana camara*

Introduction

Metals and its alloys are exposed to the action of acids in industry[1]. The exposures can be harmful in many cases, i.e. corrosion rates of metallic materials in these acids media[2-3]. Metals are usually extracted from ores through the application of a considerable amount of energy. Corrosion is simply the strong tendency of an elemental metal to revert back to its natural state[4]. Hence, corrosion is the primary means by which metals deteriorate.

These substances, which are sometimes referred to as retarding catalyst, are generally called inhibitors[5]. The use of inhibitors is one of the best methods for protecting metals against corrosion.

Corrosion is a chemical or electrochemical process in nature with four components are: an anode, a cathode, an electrolyte and some direct electrical connection between the anode and cathode, the adsorbed inhibitor then acts to slow corrosion process by either:

1. Increasing the anodic or cathodic polarization behaviour;

2. Reducing the movement or diffusion of ions to the metallic surface.

Aluminium is a reactive metal. To reduce the corrosion problem in these environment inhibitive effects of various naturally occurring substance like *Datura stramonium*[7] *Tannin beet* root, *Tamarind*, *Tealeaves*, *Pomegranate juice*, *Saponin*[8] *Embellica officinalis*, *Terminalia bellerica*, a mixture of the later three *Spindus trifolianus*, *Acacia concianna*, *Swerti aungustifolia* and quinoline based cinchona alkaloids as well as very popular ayurvadic powder *Mahasudarshana churna*, *Prosopis juliflora*[9], *Caparis decidua*[10], A*dhotoda-vasica*, *Vinca-rosea*, *Heena*[11], *Eugenia jambolans*, pomegranate and *Peels*[12-13], *Tannins*, *Caffeine*, *Prosopis cineraria*[14] and *Ficus relegeosa*[15] have been evaluated as effective corrosion inhibitiors. Generally organic compounds having heteroatom O, N and S are found to have higher basicity and electron density thus assist in corrosion inhibitor. O, N and S are the active center for the adsorption on the metal surface[16-17].

Lantadene C
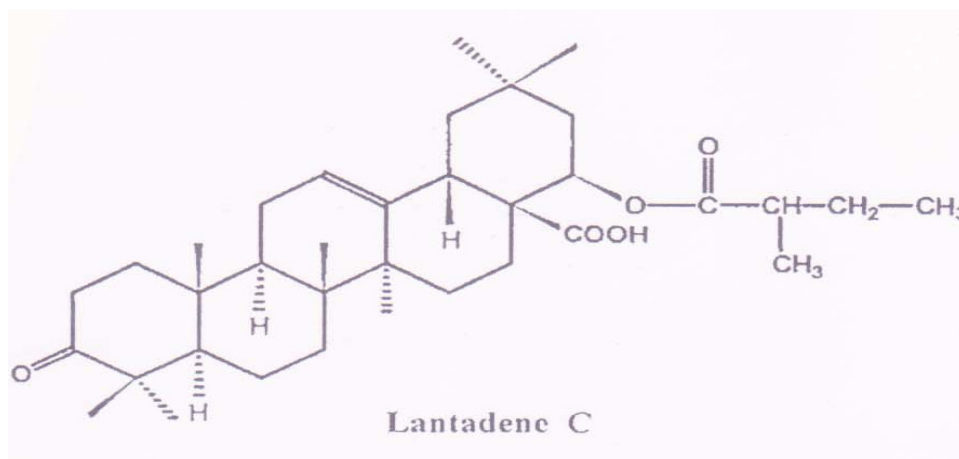
Experimental: The *Lanatana camara* plants extract were dried, then finally powdered and extracted with boiling ethanol.

Specimen preparation: Rectangular specimens of aluminium of dimension $2.5*1.5*0.02 Cm^3$ containing a small hole of 0.2 cm diameter near the upper edge were employed for the determination of corrosion rate. Specimens were cleaned by pumice powder and degreased. Each specimen was suspended by a glass hook and immersed in a beaker containing 50mL of test solution at $25 \pm 5°C$ and left exposed to air to 24 hours. Evaporation losses were made up with deionized water. After the test specimens were cleaned with acetone. Duplicate experiments were performed in each case and mean values of the mass loss were calculated.

Test solution preparation:
The acidic solution was prepared by using deionized water. All chemicals were used of analytical grade reagent.
The percentage inhibition efficiency was calculated as[18]

$$I = \frac{\Delta Mu - \Delta Mi}{\Delta Mu} \times 100 \text{-------(1)}$$

Where ΔMu and ΔMi are the mass loss of the metal is uninhibited and inhibited solution respectively.
The degree of surface coverage (θ) can be calculated as[19]

$$\theta = \frac{\Delta Mu - \Delta Mi}{\Delta Mu} \text{---------(2)}$$

Where θ surface coverage and ΔMu and ΔMi are the mass loss of the metal in uninhibited and inhibited basic solution.
The corrosion rate is mmpy (mili mile per year) can be obtained by the following equation[20].

Corrosion rate (mmpy) =
$$\frac{Weightloss \times 87.6}{Area \times Time \times Metaldensity} \text{----------(3)}$$

Where mass loss is expressed in gm, area is expressed in cm² of metal surface exposed, time is expressed in hours of exposure, metal density is expressed in gm/cm³ and

87.6 is conversion factor.
Inhibition efficiency was also determined using a thermometric technique. This involved the immersion of single specimens measuring $2.5*1.5*0.02 Cm^3$ 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 $\pm 0.5°C$. The temperature increased slowly at first then rapidly and attained a maximum temperature was recorded and the percentage inhibition efficiencies were calculated as[21]

$$\eta = \frac{(RNf - RNi)}{RNf} \times 100 \text{--------(4)}$$

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

$$RN = \frac{(Tm - To)}{t} \text{-------------(5)}$$

Where Tm and To are the maximum and initial temperature respectively and t is the time required to reach the maximum temperature.

Result and discussion:
The inhibition efficiency (%) calculated from the mass loss measurement for sulphuric acid solution and inhibitors are given in tables (1-3). It was observed that the inhibition efficiency was found to increase with increase in the concentration of inhibitor and decrease with increases in acid strength. The corrosion rate decreased with increasing concentration of the inhibitor. The inhibitors were found to show efficiency in a broad range. *Lanatana camara* showed minimum of 8.37% and maximum of 64.28% in 0.1N sulphuric acid solution while 0.2N sulphuric acid solution exhibited a minimum of 28.25% and a maximum of 57.34%.The 0.5N sulphuric acid solution showed a minimum efficiency of 24.13% and maximum of 62.38%. Inhibition efficiency (IE) values were also determined by the thermometric method in table (4). Temperature changes for aluminium in 3N, 4N and 5N sulphuric acid solution were recorded

at various inhibitor concentrations. The thermometric method was used for 3N, 4N and 5N sulphuric acid solution. *Lanatana camara* extract showed minimum and maximum IE of 26.02% and 76.36% with 2N sulphuric acid solution, 39.16% and 65.89% with 3N sulphuric acid solution 37.28% and 59.36% with 4N sulphuric acid and 33.14% , 60.58% with 5N sulphuric acid solution respectively.
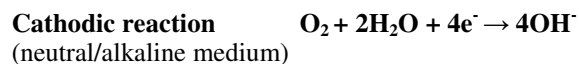
Organic corrosion inhibitors[22] function via chemisorption of the molecule on the metallic surface., complexing of the molecule with the metal ion which remains in solid state.,neutralising the corrodent or adsorbing the corrodent. Generally, the adsorption of organic molecules may block active sites hence may decrease the corrosion rate. In the present study, it is assumed that the plant extract are adsorbed on the metal surface and decreases the surface area available for cathodic and anodic reaction to takes place.

Morphological analysis

The morphology of aluminium surface was analyzed through SEM micrographs of the surface before and after immersion in sulfuric acid solutions of varying strengths. The specimens were examined under an optical microscope Model-ZEISS EVO 50. The surface morphological characteristics of the blank and inhibited aluminium were analyzed at magnification of 2.0 KX operated at an accelerating voltage of 20 KV. Figure.1 shows the aluminium surface image while figure.2 shows the morphology of aluminium surface with *Lanatana camara* fruit extract in 0.5N sulphuric acid solution

Absorption of oxygen- This type of corrosion occurs generally in aqueous solution.

The corrosion of aluminium and aluminium alloys precede through the following elementary reactions:

Anodic reaction $\quad\quad Al \rightarrow Al^{3+} + 3e^-$

Cathodic reaction $\quad\quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
(neutral/alkaline medium)
$2H^+ + 2e^- \rightarrow H_2\uparrow \quad\quad$ (acidic medium)

In the present study, it was assumed that the plant extract are adsorbed on the metal surface and decreases the surface area available for cathodic and anodic reaction to take place. The adsorbed plant extract parts act to slow corrosion process by either:

1. Increasing the anodic and/or cathodic polarization behaviour.
2. Reducing the movement or diffusion of ions to the metallic surface.
3. Increasing the electrical resistance of the metallic surface.

Surface analysis shows the plant extract adsorbed on metal surface and decrease the surface area for corrosion reaction.

CONCLUSIONS:

1. Plant inhibitors inhibited aluminium corrosion in acidic solutions.
2. Corrosion inhibition of aluminium in acidic solution is under anodic control.
3. Inhibition efficiency of plant extracts increases with increase in concentration.
4. The mass loss measurements are in good agreement with electrochemical method.
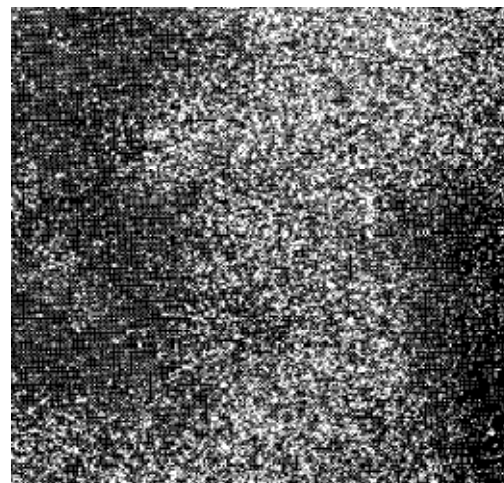
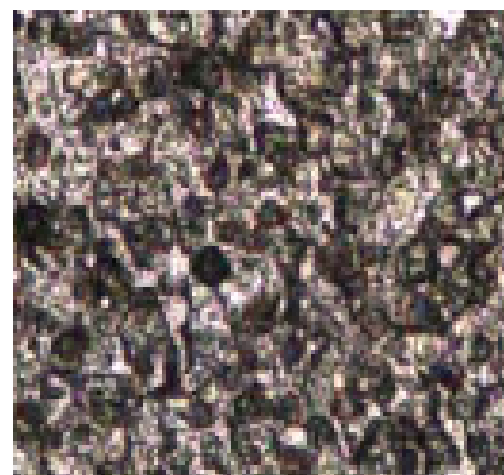Figure.1 Aluminium surface image

Figure.2 aluminium surface with *Lanatana camara* fruit extract in 0.5N sulphuric acid solution

Table-1. Mass loss data for aluminium in 0.1N sulphuric acid with ethanolic extract of leaves, stem bark and fruit of *Lanatana camara.* Effective area of specimens- 7.5 cm^2. Temperature- 25±5°C. Immersion period-24 hours.

Inhibitors Conc. (%)	Mass loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency	Surface coverage
Uninhibited	0.0752	0.0542		
		Leaves		
0.12	0.0689	0.0496	8.37	0.0837
0.24	0.0534	0.0385	28.98	0.2898
0.36	0.0499	0.0359	33.64	0.3364
0.48	0.0362	0.0260	51.86	0.5186
0.60	0.0318	0.0229	57.71	0.5771
		Stem bark		
0.12	0.0639	0.0460	15.02	0.1502
0.24	0.0651	0.0369	31.92	0.3192
0.36	0.0481	0.0346	36.03	0.3603
0.48	0.0372	0.0268	50.53	0.5053
0.60	0.0308	0.0222	59.04	0.5904
		Fruit		
0.12	0.0589	0.0392	26.43	0.2613
0.24	0.0473	0.0347	34.89	0.3489
0.36	0.0365	0.0210	55.34	0.5534
0.48	0.0301	0.0194	62.57	0.6257
0.60	0.0268	0.0183	64.28	0.6428

Table-2. Mass loss data for aluminium in 0.2N sulphuric acid with ethanolic extract of leaves, stem bark and fruit of *Lanatana camara*. Effective area of specimens- 7.5 cm^2. Temperature- 25±5°C. Immersion period-24 hours.

Inhibitors Conc. (%)	Mass loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency	Surface coverage
Uninhibited	0.0959	0.0690		
		Leaves		
0.12	0.0679	0.0489	29.19	0.2919
0.24	0.0538	0.0387	43.89	0.4389
0.36	0.0464	0.0334	51.61	0.5161
0.48	0.0432	0.0311	54.95	0.5495
0.60	0.0412	0.0297	57.03	0.5703
		Stem bark		
0.12	0.0688	0.0490	28.25	0.2825
0.24	0.0561	0.0404	41.50	0.4150
0.36	0.0492	0.0354	48.69	0.4869
0.48	0.0400	0.0317	54.11	0.5411
0.60	0.0314	0.0298	56.83	0.5683
		Fruit		
0.12	0.0653	0.0468	31.52	0.3152
0.24	0.0587	0.0581	42.62	0.4262
0.36	0.0465	0.0457	49.49	0.4949
0.48	0.0396	0.0390	55.62	0.5562
0.60	0.0309	0.0291	57.34	0.5734

Table-3. Mass loss data for aluminium in 0.5N sulphuric acid with ethanolic extract of leaves, stem bark and fruit of *Lanatana camara*.
Effective area of specimens- 7.5 cm^2. Temperature- 25±5°C. Immersion period-24 hours.

Inhibitors Conc. (%)	Mass loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency	Surface coverage
	Uninhibited	0.0033	0.0237	
		Leaves		
0.12	0.0021	0.0015	36.36	0.3636
0.24	0.0019	0.0013	42.42	0.4242
0.36	0.0016	0.0011	51.51	0.5151
0.48	0.0014	0.0010	57.57	0.5757
0.60	0.0013	0.0009	60.60	0.6060
		Stem bark		
0.12	0.0023	0.0016	30.30	0.3030
0.24	0.0020	0.0014	39.39	0.3939
0.36	0.0018	0.0012	45.45	0.4545
0.48	0.0017	0.0011	48.48	0.4848
0.60	0.0014	0.0010	57.57	0.5757
		Fruit		
0.12	0.0018	0.0012	45.46	0.4546
0.24	0.0015	0.0010	54.36	0.5436
0.36	0.0013	0.0009	60.60	0.6060
0.48	0.0011	0.0008	63.62	0.6362
0.60	0.0009	0.0007	66.74	0.6674

Table-4. Thermometric reaction for aluminium in 2N, 3N, 4N and 5N sulphuric acid with ethanolic extract of leaves, stem bark and fruit of *Lanatana camara*.
Effective area of specimens- 7.5 cm^2. Temperature- 25±5°C. Immersion period-24 hours.

Inhibitor Conc (%)	2N H_2SO_4	η %	3N H_2SO_4	η %	4N H_2SO_4	η %	5N H_2SO_4	η %
Uninhibited	2.19		4.80		6.25		7.35	
			Leaves					
0.12	1.54	29.68	2.86	40.41	3.92	37.28	4.46	39.31
0.24	1.36	37.89	2.32	51.66	3.46	44.60	4.13	43.80
0.36	1.09	50.22	1.98	58.75	3.11	50.24	3.18	48.16
0.48	0.85	61.18	1.77	63.12	2.72	56.48	3.52	52.10
0.60	0.68	68.94	1.67	65.20	2.54	59.36	2.99	59.10
			Stem bark					
0.12	1.62	26.02	2.92	39.16	3.81	39.04	4.87	33.14
0.24	1.46	33.33	2.13	55.62	3.67	41.28	4.62	37.14
0.36	1.13	48.40	1.99	58.54	3.03	51.52	4.12	43.94
0.48	0.93	57.30	1.84	61.66	2.68	57.12	3.64	50.47
0.60	0.78	64.38	1.78	62.91	2.59	58.56	3.14	57.27
			Fruit					
0.12	0.93	57.30	2.89	39.57	3.76	41.28	4.53	37.59
0.24	0.82	63.52	2.11	56.66	3.22	46.59	4.11	45.68
0.36	0.75	67.63	1.96	58.63	3.00	52.34	3.16	50.24
0.48	0.63	72.45	1.83	62.31	2.74	55.87	3.49	53.67
0.60	0.58	76.36	1.66	65.89	2.56	58.44	2.97	60.58

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