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Behavior of naturally occurring plant *Cordia Dichotoma* as corrosion inhibitor for aluminium in acidic media

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Abstract

The corrosion inhibition efficacy of alcoholic extracts of stem, leaves and fruits of *Cordia Dichotoma* towards hydrochloric acid for aluminium has been studied by using mass loss and thermometric methods. It has been observed that at constant acid concentration, the inhibition efficiency of all the extracts increases with the inhibitor concentration. At constant inhibitor concentration the inhibition efficiency decreases with the increase in acid concentration. It has been also observed that the inhibition efficacy decreases with the increase in the temperature.

Key words: *Cordia dichotoma*, Aluminium, Mass loss method, Thermometric method, corrosion inhibitor, inhibition efficiency.

Introduction

Aluminium is selected for variety of engineering applications because of lightness, strength, thermal and electrical conductivities, heat and light reflectivity and hygienic and non toxic qualities,[1] but it suffers from a serious corrosion problem causing considerable revenue loss throughout the world.[2] Aluminium is known to exhibit passive behaviour in aqueous solutions, but dissolves in aqueous acids with liberation of hydrogen gas.[3]

There are varieties of synthetic corrosion inhibitors available but our present focous on the naturally occurring inhibitors which are eco-friendly, eonomic and having no toxic effects without affecting the natural properties of metal. Numerous naturally occurring products such as *Prosopis juliflora*,[4] *Eugenia jambolans*,[5] *Lawsonia* extract,[6] *Opuntia* extract,[7] *Swertia aungustifolia*,[8] *Ficus religeosa*,[9] *Heena*,[10] *Datura stromonium*,[11] and *Calotropis* plants [12] have been evaluated as potential corrosion inhibitors. We present here our present study on the inhibitive action of alcoholic extracts of stem, leaves and fruits of *Cordia Dichotoma* on the corrosion of aluminium in presence of acidic media.

Plant Introduction - *Cordia dicotoma* belongs to family Boraginaceae. Its common name is Indian cherry, lasura. Its chemical constitutions are mono and polysachharides, Beta-

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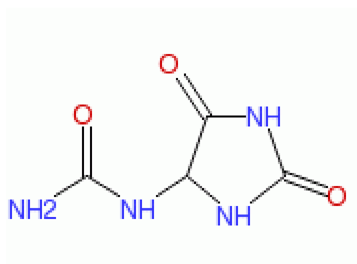
sitosterol, flavonol glycoside, taxifotin, 3-rhamnoside, 3-5-dirhamnoside, distylin, 3-xyloside, allantoin. It is Astringent, anthelmintic, diuretic, demulcent and expectorant (fruit) and useful in the cough, chest diseases hence it relieves from severe colic pain. *Cordia dichotoma* contains a large number of alkaloids containing oxygen and nitrogen, out of which Allantoin (Fig. 1) predominates which is effective for corrosion inhibition activity in acidic media for aluminium.



(Fig. 1)

Allantoin

Experimental

MASS LOSS MEASUREMENTS:

Specimen preparation

Rectangular specimens of iron of dimensions 2.54 x 1.52 x .02 cm with a small hole of about 2mm diameter near the upper edge were employed for the determination of mass loss measurements. Specimens were cleaned by buffing to produce mirror finish with the help of emery paper and were then degreased with acetone. Each specimen was suspended by a glass hook and immersed in a beaker

JCSE The Journal of Corrosion Science and Engineering
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containing 50 mL of test solution and left expose to air. Duplicate experiments were performed in each case and mean value of mass losses were calculated.

Test solution preparation

The hydrochloric acid solutions of 0.5N, 1.0 N and 2.0 N were prepared using doubly distilled water. The extracts of different parts of *Cordia dichotoma* were obtained by refluxing respective part in a soxhlet in ethanol.

To observe the influence of various parameters like inhibitor concentration, acid concentration and time, the corrosion inhibition efficiency (η %) of the compounds have been calculated by mass loss method using following equation.[13]

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

Where Δ Mu is mass loss without inhibitor and Δ Mi is mass loss with inhibitor. The degree of surface coverage (θ) can be calculated as –

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

The corrosion rate in millimeter penetration per year (mmpy) can be obtained by following equation. [14]

$$\text{Corrosion rate (mmpy)} = (\Delta M \times 87.6) / \text{area} \times \text{time} \times \text{metal density}$$

Where Δ M mass loss expressed in mg, area expressed in square cms of metal surface exposed, time expressed in hours of exposure and metal density expressed in g / cm^3.

THERMOMETRIC MEASUREMENTS:

Inhibition efficiencies were also determined by thermometric method. [15] In this method, the variation of temperature is followed as a function of time. The specimens of size 2.54 x 1.52 x .02 cm were immersed in 50mLof acid solution. The tests were carried out in different concentrations of HCl solutions. The inhibition studies were carried out in the concentrations 0.12%, 0.24%, 0.36% 0.48% and 0.60% of the extract of *Cordia dichotoma,* and observations were carried out in an insulated chamber. The results were used to calculate Reaction

JCSE The Journal of Corrosion Science and Engineering
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Number (R.N.) and inhibition efficiency (*η %)*. Reaction Number can be calculated by the following equation-

$$RN = (Tm - Ti) / t$$

Where Tm and Ti are initial and maximum temperatures respectively and t is the time in minutes to attain Tm during the observations. The inhibition efficiency can be calculated as –

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

Where RN_{free} and RNi are Reaction Number in blank and inhibited system respectively.

E_a has been calculated from the Arrhenius equation.

$$\text{Log } P_2/P_1 = E_a / 2.303\, R\, (1/T_1 – 1/T_2)$$

Where P_1 and P_2 are the corrosion rate at temperature T_1 and T_2 respectively. The values of heat of adsorption (Q_{ads}) were calculated by the following equation.[16]

$$Q_{ads} = 2.303\, R\, [\log (\theta_2 / 1 - \theta_2) - \log (\theta_1 / 1 - \theta_1)] \times [\, T_1.T_2 / (T_2 - T_1)\,]$$

Where θ_1 and θ_2 [$\theta = (\Delta Mu - \Delta Mi) / \Delta Mu$] are the fraction of the metal surface covered by the inhibitors at temperature T_1 and T_2 respectively. The values of heat of adsorption (ΔG^0_{ads}) were calculated from slope of the plot of the following equation. [17]

$$\log C = \log (\theta / 1 - \theta) – \log B$$

where $\log B = -1.74 - (\Delta G^0_{ads} / 2.303\, RT)$, and C is the inhibitor concentration.

The ΔH^0_{ads} and ΔS^0_{ads} were calculated using the following equations.

$$\Delta H^0_{ads} = E_a - R\, T$$

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

JCSE The Journal of Corrosion Science and Engineering
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Table - 1

Effect of temperature on Mass loss and inhibition efficiency (*η %)* for Aluminium in 0.5 N HCl with given inhibitor addition.

Area of exposure – 7.75 cm^2 **Time of exposure - 18hrs**

Inhibitorconcentration(%)	300 K			290 K		
	Δ M, (g)	(*θ*)	*η %*	ΔM, (g)	(*θ*)	*η %*
Fruit extract						
Uninhibited	0.121			0.119		
0.12	0.024	0.801653	80.16529	0.014	0.882353	88.23529
0.24	0.021	0.826446	82.64463	0.012	0.89916	89.91597
0.36	0.02	0.834711	83.47107	0.011	0.907563	90.7563
0.48	0.019	0.842975	84.29752	0.007	0.941176	94.11765
0.60	0.01	0.917355	91.73554	0.004	0.966387	96.63866
Leaves extract						
Uninhibited	0.121			0.119		
0.12	0.025	0.793388	79.33884	0.016	0.865546	86.55462
0.24	0.022	0.818182	81.81818	0.013	0.890756	89.07563
0.36	0.021	0.826446	82.64463	0.012	0.89916	89.91597
0.48	0.019	0.842975	84.29752	0.009	0.92437	92.43697
0.60	0.013	0.892562	89.2562	0.006	0.94958	94.95798
Stem extract						
Uninhibited	0.121			0.119		
0.12	0.027	0.77686	77.68595	0.017	0.857143	85.71429
0.24	0.024	0.801653	80.16529	0.014	0.882353	88.23529
0.36	0.023	0.809917	80.99174	0.012	0.89916	89.91597
0.48	0.022	0.818182	81.81818	0.01	0.915966	91.59664
0.60	0.014	0.884298	88.42975	0.007	0.941176	94.11765

JCSE The Journal of Corrosion Science and Engineering
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Table - 2

Effect of acid concentration on Mass loss and inhibition efficiency (*η %)* for Aluminium at 300 ± 0.1 K with given inhibitor addition.

Area of exposure – 7.75 cm^2 **Time of exposure - 18hrs**

Inhibitor concentration (%)	0.5N HCl		1.0 N HCl		2.0N HCl	
	ΔM (g)	*η %*	**ΔM (g)**	***η %***	**Δ M, (g)**	***η %***
Fruit extract						
Uninhibited	0.121		0.132		0.185	
0.12	0.024	80.16529	0.032	75.75758	0.059	68.10811
0.24	0.021	82.64463	0.03	77.27273	0.052	71.89189
0.36	0.02	83.47107	0.028	78.78788	0.047	74.59459
0.48	0.019	84.29752	0.024	81.81818	0.039	78.91892
0.60	0.01	91.73554	0.017	87.12121	0.036	80.54054
Leaves extract						
Uninhibited	0.121		0.132		0.185	
0.12	0.025	79.33884	0.035	73.48485	0.062	66.48649
0.24	0.022	81.81818	0.031	76.51515	0.053	71.35135
0.36	0.021	82.64463	0.03	77.27273	0.049	73.51351
0.48	0.019	84.29752	0.027	79.54545	0.043	76.75676
0.60	0.013	89.2562	0.019	85.60606	0.037	80
Stem extract						
Uninhibited	0.121		0.132		0.185	
0.12	0.027	77.68595	0.036	72.72727	0.066	64.32432
0.24	0.024	80.16529	0.032	75.75758	0.057	69.18919
0.36	0.023	80.99174	0.031	76.51515	0.052	71.89189
0.48	0.022	81.81818	0.03	77.27273	0.049	73.51351
0.60	0.014	88.42975	0.021	84.09091	0.039	78.91892

JCSE The Journal of Corrosion Science and Engineering

ISSN 1466-8858 Volume 13, Preprint 12 submitted 18 February 2010

Table - 3

Corrosion rate, Activation energy (E_a), Heat of adsorption (Q_{ads}), and free energy of adsorption (ΔG^0_{ads}) for Aluminium in 0.5 N HCl with given inhibitor addition at 300 ± 0.1 K.

Area of exposure – 7.75 cm^2 **Time of exposure – 18 hrs**

S.No.	Inhibitor concentration (%)	Corrosion rate	(E_a) (KJ /mol)	(Q_{ads}) (KJ /mol)	(ΔG^0_{ads}) (KJ/mol)	ΔH^0_{ads} (KJ/mol)	ΔS^0_{ads} (J/ mol / K)
Fruit extract							
1	BLANK	0.03	0.0159			-2492.98	
2	0.12	0.005586	0.514936237	-1434.85	-18.75926	-2492.49	-2492.42
3	0.24	0.004888	0.5346351	-1714.90	-17.43983	-2492.47	-2492.41
4	0.36	0.004655	0.571150156	-1897.23	-16.5753	-2492.43	-2492.37
5	0.48	0.004422	0.953955503	-3178.40	-16.01044	-2492.05	-2491.99
6	0. 60	0.002327	0.875388431	-5766.71	-17.2653	-2492.12	-2492.07
Leave extract							
1	BLANK	0.028163	0.0159			-2492.98	
2	0.12	0.005819	0.426365293	-1218.31	-18.63163	-2492.57	-2492.51
3	0.24	0.005120	0.502608827	-1561.23	-17.29879	-2492.5	-2492.44
4	0.36	0.004888	0.5346351	-1714.90	-16.42883	-2492.47	-2492.41
5	0.48	0.004422	0.713859499	-2392.11	-16.01044	-2492.29	-2492.23
6	0. 60	0.003026	0.738675466	-3728.72	-16.5428	-2492.26	-2492.21
Stem extract							
1	BLANK	0.028163	0.0159			-2492.98	
2	0.12	0.006284	0.441972471	-1136.11	-18.38725	-2492.56	-2492.50
3	0.24	0.005586	0.514936237	-1434.85	-17.03094	-2492.49	-2492.43
4	0.36	0.005353	0.621545989	-1724.95	-16.15162	-2492.38	-2492.32
5	0.48	0.005120	0.753261413	-2132.82	-15.57046	-2492.25	-2492.20
6	0. 60	0.003258	0.662205784	-3146.47	-16.33483	-2492.34	-2492.28

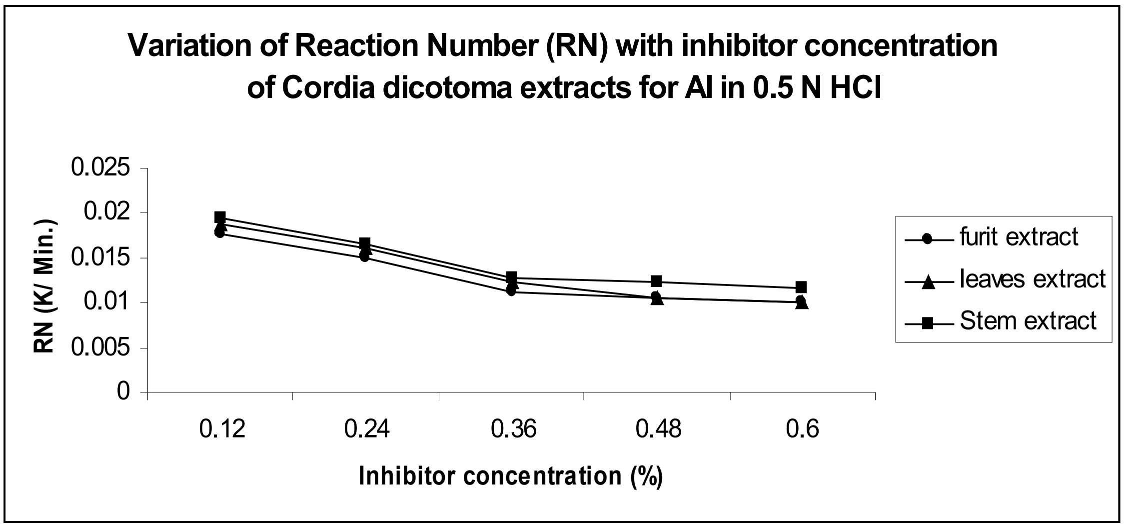
JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 13, Preprint 12 submitted 18 February 2010

Table – 4

Reaction Number (RN) and Inhibition efficiency (η %) for Aluminium in 0.5 N and 1.0 N HCl solution with given inhibitor addition at 299 ± 0.2 K

Area of exposure – 7.75 cm^2 **Time of exposure – 18 hrs**

Inhibitor concentration (%)	0.5 N HCl		1.0 N HCl	
	RN	η %	RN	η %
Uninhibited	0.075	-	0.078	-
Fruit extract				
0.12	0.017778	76.2963	0.020556	73.9437
0.24	0.015	80	0.017222	78.16904
0.36	0.011111	85.18519	0.013333	83.09862
0.48	0.010556	85.92593	0.011667	85.21129
0.60	0.01	86.66667	0.011111	85.91551
Leave extract				
0.12	0.018889	74.81481	0.022222	71.83103
0.24	0.016111	78.51852	0.018889	76.05637
0.36	0.012222	83.7037	0.015	80.98594
0.48	0.010556	85.92593	0.012778	83.80284
0.60	0.01	86.66667	0.011667	85.21129
Stem extract				
0.12	0.019444	74.07407	0.024444	69.01413
0.24	0.016667	77.77778	0.022778	71.1268
0.36	0.012778	82.96296	0.020556	73.9437
0.48	0.012222	83.7037	0.017222	78.16904
0.60	0.011667	84.44444	0.013889	82.39439


Variation of Reaction Number (RN) with inhibitor concentration of Cordia dicotoma extracts for Al in 0.5 N HCl
RN (K/ Min.)
0.025
0.02
0.015
0.01
0.005
0
0.12
0.24
0.36
0.48
0.6
Inhibitor concentration (%)
furit extract
leaves extract
Stem extract

JCSE The Journal of Corrosion Science and Engineering
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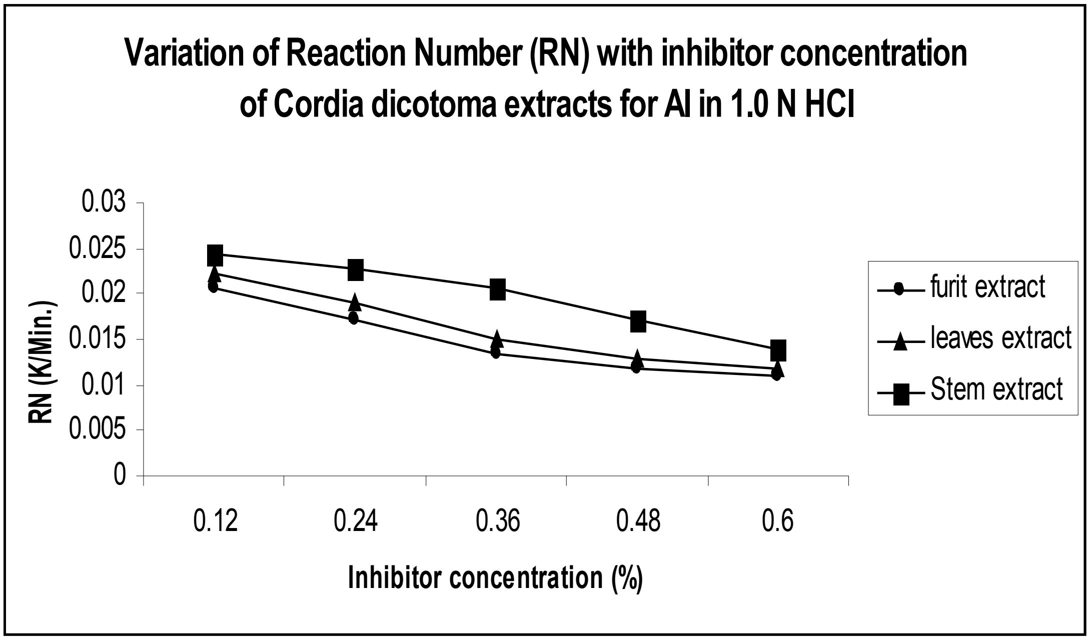

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 13, Preprint 12 submitted 18 February 2010

Result and discussion

The results are presented in Table 1-4, and Fig. 1-2. The effect of temperature on the corrosion of aluminium is shown in Table -1. It shows that corrosion rate is increased with the temperature and the inhibition efficiency decreases with the increase in temperature. The corrosion rate may be increased with temperature due to thermal activated kinetics. [18]

The effect of acid concentration on the corrosion of aluminium is shown in Table -2. It shows that the I.E. decreases with increase in the acid concentration. At constant acid concentration the I.E. increases with increase in the inhibitor concentration, e.g. in 0.5N HCl the I.E. was found to be 80.16, 82.64, 83.47, 84.29 and 91.73 % with respect to 0.12, 0.24, 0.36, 0.48 and 0.60 inhibitor concentration (fruit extract) (Table - 2).

For all acid concentrations the inhibition efficiency of alcoholic extracts of fruit, leaves and stem of *Cordia dichotoma* was calculated by massloss and thermometric methods, and it was observed that the fruit extract shows the maximum inhibition efficiency at both the temperatures. (Table 1, 2and 4).

From Table -3 it is evident that in all cases the values of Q_{ads} are negative (- 1434.85 to -3146.47) . The negative values shows that the adsorption, and hence the inhibition efficiency, decreases with a rise in temperature. [19]

The negative values of ΔG^o_{ads} ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. Generally, values of ΔG^0_{ads} lower than – 40 KJ/mol is consistant with the electrostatic interaction between the charged molecules and the charged metal (physisorption) ; those around -50 KJ/mol or higher involve charge shairing or charge transfer from organic molecule to the metal surface to form a coordinate bond (chemisorption) [20,21]. In the present work, the calculated values of ΔG^o_{ads} are lower than –40 kJ mol^{-1}, indicating, therefore that the adsorption mechanism of extracts of *Cordia dicotoma* on metal surface in 0.5 N HCl solution was typical of physisorption (Table 3).

The enthalpy changes are negative (Table 3) means that heat is released from the adsorption process. Generally, an exothermic adsorption process signifies either physi- or chemi-sorption, while endothermic process is attributable unequivocally to chemi-sorption 22. The absolute value of the adsorption enthalpyΔH^0_{ads}, increases with the increase in surface coverage and the inhibitor concentration due to the attractive interaction between the adsorbed molecules indicating the validity of the Temkin model [23].

JCSE The Journal of Corrosion Science and Engineering
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Large and negative values of the entropy (Table 3) imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [24,25]
The increase in E_a^o (Table 3) is proportional to the inhibitor concentration, indicating that the energy barrier for the corrosion interaction is also increased [26,27]. This means that the corrosion reaction will be further pushed to the surface sights that are characterised by progressively higher values of E_a^o as the concentration of the inhibitor in the solution becomes larger. In other words, the adsorption of the inhibitor on the metal surface leads to the formation of a physical barrier that reduces the metal reactivity in the electrochemical reactions of corrosion [28].

From (Table 4) it is concluded that the Reaction Number (RN) decreases with the increase in the inhibitor concentration while the inhibition efficiency increases with the inhibitor concentration.

Conclusions

In the present work, mass loss and thermometric methods were used to study the effect of temperature on the ability of extracts of *Cordia dichotoma* to inhibit the corrosion of aluminium in acidic conditions. The principle conclusions are:

- The rate of corrosion decreases with increase in the inhibitor concentration.
- The corrosion rate increases and the inhibition efficiency decreases with the increase in temperature.
- The fruit extract of *Cordia dichotoma* shows the maximum inhibition efficiency as compered to the leaves and stem extracts.
- The thermodynamic parameters revealed that the inhibition of corrosion by extracts of *Cordia dichotoma* is due to the formation of a physisorbed film of the inhibitor on the metal surface.
- The inhibition efficiency (IE%) of extract of *Cordia dichotoma* was temperature-dependent and its addition led to an increase of the activation corrosion energy.

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