Study of Plant *Cordia Dichotoma* as Green Corrosion Inhibitor for Mild Steel in Different Acid Media

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Abstract: The corrosion inhibition of mild steel using extracts of *Cordia dichotoma* in different acid media was investigated by mass loss and thermometric methods. The experiments were carried out at 299 ± 0.2 K in presence of different concentrations of dry fruit, leaves and stem extracts of *Cordia dichotoma*. The results reveal that the alcoholic extracts of *Cordia dichotoma* is a better corrosion inhibitor than that of toxic chemicals. The fruit extract is more potent than leaves and stem extracts to inhibit the corrosion rate. The study seeks to investigate the possibility of using extracts of *Cordia dichotoma* as a green corrosion inhibitor for mild steel.

Keywords: *Cordia dichotoma*, Mild steel, Mass loss method, Thermometric method, Green corrosion inhibitor, Inhibition efficacy.

Introduction

Mild steel, the most commonly used metal; usually it is selected for many mechanical and engineering purposes due to its properties such as strength, ease of fabrication and cost. But the main disadvantage with its use is that it undergoes rapid corrosion in acidic medium. Concentrated mineral acids are used extensively in pickling, cleaning and oil well acidising of metallic material cause corrosion^{1,2}. It has been speculated that organic compounds containing nitrogen and oxygen are good inhibitors for mild steel in acid medium³. There are many substances available for this purpose but our present focus is on the naturally occurring green inhibitors, which are ecofriendly, less expensive and having no side effects. Numerous naturally occurring products such as *Prosopis juliflora*⁴, *Eugenia jambolans*⁵, *Lawsonia*⁶, *opuntia*⁷, *Swertia aungustifolia*⁸, *Ficus religiosa*⁹, *heena*¹⁰, *Datura stromonium*¹¹ and *calotropis* plant extracts¹² have been evaluated as potential corrosion inhibitors. We report here our present study on the inhibitive action of alcoholic extracts of stem, leaves and fruits of *Cordia dichotoma* on the corrosion of mild steel in presence of acidic media.

Description of inhibitor

Cordia dichotoma belongs to family boraginaceae. Its common name is Indian cherry, lasura. Its chemical constitutions are mono and polysachharides, *beta*-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 relief from severe colic pain. The alkaloid - Allantoin (Figure 1) present in *Cordia dichotoma* is found to be effective for corrosion inhibition activity in acidic media for mild steel.

Figure 1. Allantoin

Experimental

According to ASTM as reported already¹³ rectangular specimens of mild steel of dimensions 2.55 x 1.50 x 0.02 cm with a small hole of about 2 mm 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 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 and sulfuric acid solutions of 1.0 N were prepared using doubly distilled water. The extracts of different parts of *cordia dicotoma* 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 ($\eta\%$) of the compounds have been calculated by mass loss method using following equation¹⁴.

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

Where ΔM_u is mass loss without inhibitor and ΔM_i is mass loss with inhibitor. The degree of surface coverage (θ) can be calculated as:

$$(\theta) = (\Delta M_u - \Delta M_i) / \Delta M_u$$

The corrosion rate in millimeter penetration per year (mmpy) can be obtained by following equation¹⁵. Corrosion rate (mmpy) = $(\Delta M \times 87.6) / \text{area} \times \text{time} \times \text{metal density}$. Where ΔM 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 / cm³.

Thermometric measurements

Inhibition efficiencies were also determined by thermometric method¹⁶. In this method, the variation of temperature is followed as a function of time. The specimens of size 2.54x1.52x.02 cm were immersed in 50 mL of 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 number (RN) and inhibition efficiency ($\eta\%$). Reaction number can be calculated by the following equation-

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

Where T_m and T_i are initial and maximum temperatures respectively and 't' is the time in minutes to attain T_m during the observations. The inhibition efficiency can be calculated as:

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

Where, RN_{free} and RN_i are reaction numbers in blank and inhibited system respectively.

Results and Discussion

Effect of inhibitor concentration

The inhibition efficacy calculated from the mass loss and thermometric methods for different concentration of HCl, H_2SO_4 and acid mixture solutions are shown in Table 1 and 2. The results showed that the inhibition efficacy increases with the increase in inhibitor concentration for all the three acids. The results revealed that all the three extracts show maximum inhibition efficiency at their highest concentration *i.e.* 0.60%. The stem extract of 0.60% concentration shows maximum IE 93.48% in 0.1 N sulphuric acid.

Effect of acid

The inhibition efficacy calculated from the mass loss method for different acids like HCl, H_2SO_4 and mixture of acids. The results showed that the different extracts of *Cordia dichotoma* shows higher inhibition efficacy in presence of H_2SO_4 solutions as compared to the hydrochloric acid and mixture of acids. The maximum inhibition efficiency is 93.48% in 0.1 N H_2SO_4 solution for 0.60% concentration of inhibitor (stem extract).

Table 1. Mass loss and inhibition efficiency for mild steel in different acid solution with alcoholic extracts of plant *Cordia dichotoma* at 299 ± 0.2 K (Area of exposure - 7.75 cm^2 Time of exposure - 18 h)

S.No.	Inhibitor concentration, %	0.1 N HCl		0.1 N H_2SO_4		0.1N (HCl + H_2SO_4)	
	Fruit extract	M	η , %	M	η , %	M	η , %
1	Blank	0.058		0.445		0.421	
2	0.12	0.033	43.10	0.065	85.39	0.091	78.38
3	0.24	0.030	48.28	0.058	86.97	0.082	80.52
4	0.36	0.024	58.62	0.050	88.76	0.062	85.27
5	0.48	0.022	62.07	0.041	90.79	0.047	88.84
6	0.60	0.014	75.86	0.032	92.81	0.032	92.39
	Leaves extract						
1	Blank	0.058		0.445		0.421	
2	0.12	0.034	41.37	0.078	82.48	0.095	77.43
3	0.24	0.031	46.55	0.070	84.27	0.088	79.10
4	0.36	0.028	51.72	0.066	85.17	0.064	84.79
5	0.48	0.027	53.45	0.053	88.09	0.049	88.36
6	0.60	0.019	67.24	0.030	93.25	0.037	91.21
	Stem extract						
1	Blank	0.058		0.445		0.421	
2	0.12	0.057	1.72	0.041	90.79	0.101	76.01
3	0.24	0.055	5.17	0.034	92.36	0.097	76.96
4	0.36	0.051	12.06	0.033	92.58	0.075	82.18
5	0.48	0.042	27.59	0.030	93.26	0.053	87.41
6	0.60	0.031	46.55	0.029	93.48	0.042	89.39

Table 2. Reaction number (RN) and inhibition efficiency ($\eta\%$) for mild steel in H_2SO_4 at 299 ± 0.2 K with alcoholic extract of plant *Cordia dicotoma* (Area of exposure – 7.75 cm^2 Time of exposure – 24 h)

S.No	Inhibitor conc., %	3 N H_2SO_4		2 N H_2SO_4		1 N H_2SO_4	
		(RN)	η , %	(RN)	η , %	(RN)	η , %
1	Blank	0.0737		0.0716		0.0679	
Fruits extract							
2	0.12	0.0204	72.31	0.0212	70.34	0.0204	69.93
3	0.24	0.0162	77.96	0.0191	73.25	0.0162	76.07
4	0.36	0.0141	80.79	0.0154	78.48	0.0133	80.36
5	0.48	0.0137	81.35	0.0133	81.39	0.0104	84.66
6	0.60	0.0120	83.61	0.0120	83.13	0.0091	86.50
Leaves extract							
2	0.12	0.0216	70.62	0.0220	69.18	0.0212	68.71
3	0.24	0.0175	76.27	0.0204	71.51	0.0170	74.84
4	0.36	0.0158	78.53	0.0162	77.32	0.0145	78.52
5	0.48	0.0145	80.22	0.0145	79.65	0.0112	83.43
6	0.60	0.0129	82.48	0.0129	81.97	0.0100	85.27
Stem extract							
2	0.12	0.0220	70.05	0.0237	66.86	0.0220	67.48
3	0.24	0.0191	74.01	0.0212	70.34	0.0187	72.39
4	0.36	0.0170	76.83	0.0175	75.58	0.0154	77.30
5	0.48	0.0154	79.09	0.0158	77.90	0.0116	82.82
6	0.60	0.0133	81.92	0.0137	80.81	0.0108	84.04

The inhibition efficacy calculated from the thermometric method for different concentrations of H_2SO_4 . It is concluded from the results that as the concentration of acid increases the inhibition efficiency decreases and the RN increases (Table 2).

According to Langmuir the adsorbed layer is unimolecular *i.e.* there is no interaction between adsorbate and adsorbent molecule. Only then the gradient is unity but in actual practice there is an interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecule that is why the gradient is not unity. Variation of $\log(\theta)/(1-\theta)$ and $\log C$ is shown in Figure 2.

Figure 2. Longmuir adsorption isotherm for mild steel in 2.0 N ($\text{HCl}+\text{H}_2\text{SO}_4$) with alcoholic extracts of *Cordia dicotoma* (24 h)

The efficiencies of inhibitors expressed as the relative reduction in corrosion rate can be quantitatively related to the amount of adsorbed inhibitors on the metal surface. It is assumed that the corrosion reactions are prevented from occurring over the active sites of the metal surface covered by adsorbed inhibitor, whereas the corrosion reactions occurs normally on the inhibitors free area. The inhibition efficiency is then directly proportional to the fraction of surface covered with adsorbed inhibitor. This assumption has been applied to deduce the effect of concentration on adsorption of inhibitors.

Generally the adsorption of organic molecules on metallic surface involves O, N and S atoms. In the case of plant extracts of *Cordia dichotoma*, the N and O of the alkaloids may be responsible for adsorption. This process may block the active sites on metal surface, hence decreasing the rate of corrosion. Due to the higher electron density the N atom of the alkaloid acts as the reaction centre, resulting in the formation of a monolayer on the metal surface. Organic inhibitors with active portions generally contain large hydrocarbon chains or rings with positively charged amine N group at the one end. In acids and water the terminal primary, secondary and tertiary amines groups take additional hydrogen that gives them a net cationic charge. The polar amine group is adsorbed on the metal and hydrocarbon portion forms an oily water repellent surface film. The molecular dissymmetry helps these materials to act as surfactants and can stabilize emulsions of oil and water. The Organic corrosion inhibitor may function by the following factors:

- Chemisorption on the metallic surface.
- Neutralizing the corroder
- Adsorbing the corroder

They offer large coverage due to the long hydrocarbon chain and by the presence of -NH groups. Being hydrophilic in nature, the -NH group counteracted the effects of chain length and ensured higher solubility. It has been observed that the fruit extract of *Cordia dichotoma* has maximum inhibition efficiency as compared to leaves and stem extracts. This may be attributed to the presence of alkaloids. In the fruit extract the electron repelling hydroxyl group on the alkaloid is present; as a result the electron density at the N atom becomes more than the any other additives. This process increased the adsorptivity of the fruit extract on the corroding site of the metal. This explains the higher inhibition efficacy displayed by the fruit extract for 0.6% concentration.

Conclusion

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

- The inhibition efficiency increases with the increase in the inhibitor concentration.
- The corrosion rate increases and the inhibition efficiency decreases with the increase in acid concentration.
- It is anticipated that the proposed investigation on green corrosion inhibitor may be useful for preventing losses caused due to corrosion without causing any harm to the environment.

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