

Inhibition Action of Mild Steel Corrosion in HCl Acid Medium by Extract of *Digera Muricata*

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Abstract: The acid extract of *Digera muricata* is controlling the corrosion of mild steel in 1M HCl has been studied by weight loss method and electrochemical impedance spectroscopy in the absence and presence of *Digera muricata* extract at different time interval and temperature. The inhibition efficiency increases with increase the concentration of *Digera muricata* extract and immersion period. The inhibition efficiency increased with increasing temperature. The negative value of the free energy of adsorption indicates spontaneous adsorption. The *Digera muricata* extract obeys Temkin and Frenmdlich adsorption isotherm. All the reported *Digera muricata* extract was found to inhibit the corrosion of mild steel in HCl acid media.

Keywords: corrosion inhibitor, Mild steel, Plant extract, Temkin and Frenmdlich adsorption, Weight loss method.

1. Introduction

Corrosion is the deterioration of a metal by chemical or electrochemical reaction with its environment. It is impossible to eliminate corrosion completely. So prevention would be more practical than elimination. There are several methods to effectively control and minimize corrosion. The small quantity of corrosion inhibitors can delay effectively or even cancel the corrosion process. Mild steel is a material of choice in industries due to easy availability and fabrication of machineries. It comes in contact with any acid it would be rusted. Hydrochloric acid has been widely used in pickling baths and descaling operations. Hence HCl was the chosen medium. Recently, the extracts of many common plants such as polyalthia longifolia¹, Euphorbia hirta², Asafoetida³ etc., reported to be effective acid corrosion inhibitors because of their biodegradability and eco-friendliness. Plant extracts are incredibly rich sources of naturally synthesized chemical compounds (glucosinolates, alkaloids, polyphenols, tannins) and most are known to have inhibitive action. The corrosion inhibitors for different metals have been reported by several authors⁴⁻¹⁰. Generally, organic compounds containing hetero atoms like O, N and S are normally found to have higher electron density which assists in inhibitor to reduce the corrosion of mild steel. Hydrochloric acid extract of *Digera muricata* was subjected to preliminary phyto- chemical¹¹⁻¹³ testing for the detection of bioactive ingredients such as alkaloid, glucoside, terpenoid, falavanoidnd steroid. Hence, the acid extracts of *Digera muricata* as good anticorrosion inhibitor on mild steel in Hydrochloric acid medium.

2. Methods and Materials

2.1 Preparation of Plant Extract

An acid extract of DM was prepared by boiling 50g of shade dried and crushed leaves of DM with 1000 ml of 1 M HCl for 3 hours and leaving it overnight. Next day it filtered and the filtrate volume was made up to 1000 ml using the same 1M HCl.

a) Specimen Preparation

Rectangular mild steel strips of size 1 × 5 × 0.2 cm with 2mm diameter hole near the upper edge of the specimens, were degreased with acetone, rinsed with distilled water, polished to mirror finish, finally dried with filter paper and stored in desiccators.

b) Preparation of test media

The mild steel specimens were weighed and immersed in 100 ml of acid solution with help of glass hooks, without and with inhibitor at different concentrations (0.1 to 0.9%).

c) Weight Loss Measurements

Experiments were carried out in 1M HCl at 303K temperature for 0.5, 2, 4, 6, 8 and 24 hours respectively. Corrosion inhibition studies were also carried out different temperature (303K, 313K, 323K, 333K, and 343K). The weight of the specimen before and after immersion was determined. The inhibition efficiency (IE) was calculated using the following formula.

$$IE(\%) = \frac{W_u - W_i}{W_u} \times 100 \quad (1)$$

W_u - corrosion rate in the absence of inhibitor

W_i - corrosion rate in the presence of inhibitor

2.2 Electrochemical Method

Potentiodynamic measurement-Tafel polarization curves were recorded using computerized Solartron model 1284. Polarization experiment carried out in a polarization cell containing platinum electrode(auxiliary), calomel electrode(reference) and MS specimens(working electrodes) which were immersed in acidic medium in the presence and absence of different concentration of the inhibitor.

Tafel method

$$IE\% = \frac{[I_{corr}(b) - I_{corr}(I)]}{I_{corr}(b)} \times 100 \quad (2)$$

$I_{corr}(b)$ - Corrosion current without inhibitor

$I_{corr}(I)$ - Corrosion current with inhibitor

LPR method

$$IE\% = \frac{[R_p(b) - R_p(I)]}{R_p(b)} \times 100 \quad (3) \quad R_p(b)$$

$R_p(b)$ – Resistant polarization without inhibitor

$R_p(I)$ – Resistant polarization with inhibitor

3. Result and Discussion**3.1 Phytochemical Screening**

The results obtained from phytochemical screening of extract are displayed in Table 1

Table 1: Phytochemical screening of extract of DM

Plant	Digeria Muricata
Tannins	-
Alkaloids	+
Terpenoids	+
Glycosides	+
Flavanoids	-
Saponins	+
Carbohydrate	+
Steroids	-
Triterpenoids	+
Protein	+

Note: (+) - presence and (-) - absence

3.2 Weight Loss Measurements**Corrosion Rate**

The effect of inhibitor concentration on the corrosion rate of mild steel in 1M HCl in the absence and presence of different concentration of DM using weight loss method is shown in Table 2.

Table 2: Corrosion Rate of DM extract on mild steel in 1M HCl at different immersion periods from weight loss method at room temperature

Conc (% v/v)	CR(mpy)					
	1/2 Hours	2Hours	4Hours	6Hours	8Hours	24Hours
B	156.03	118.69	129.84	164.02	206.18	297.06
0.1	66.87	46.25	21.18	25.63	72.72	131.88
0.2	60.18	44.02	16.72	20.25	69.24	119.34
0.3	49.04	35.11	16.16	18.76	52.52	99.55
0.4	47.92	33.44	15.05	18.02	36.92	91.48
0.5	44.13	28.00	12.54	14.86	27.44	75.69
0.6	33.44	18.39	10.03	10.53	20.38	58.65
0.7	22.29	9.97	8.92	7.99	17.41	52.61
0.8	26.75	13.37	11.70	14.12	33.85	60.51
0.9	28.98	20.06	11.15	15.42	49.04	72.77

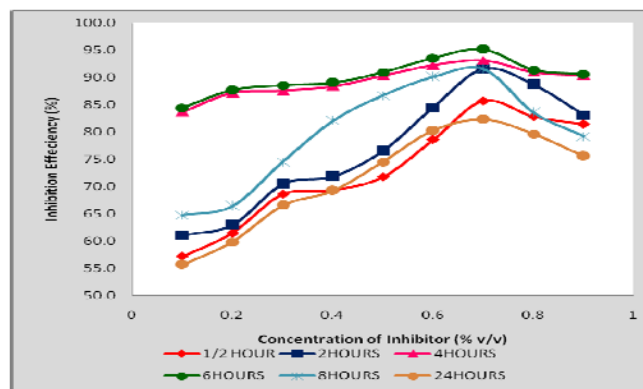
3.3 Inhibition Efficiency

The percentage of inhibition efficiency increases with increase in the extract concentration over the entire concentration range studied in all the cases. The maximum inhibition efficiency of the extract was found to be 98.7% at a concentration of 0.7% and further increase in concentration did not cause any appreciable change in the performance of inhibitor. The maximum inhibition efficiency was observed

for 4 hours of contact at 303K temperature.

Table 3: Inhibition efficiency of DM extract on mild steel in 1M HCl at different immersion periods from weight loss method at room temperature

Conc. (%v / v)		Inhibition efficiency (%)					
		1/2 Hr	2Hrs	4Hrs	6Hrs	8Hrs	24Hrs
0.1	IE(%)	57.1	61.0	83.7	84.4	64.7	55.6
	θ	0.571	0.610	0.837	0.844	0.647	0.556
0.2	IE(%)	61.4	62.9	87.1	87.7	66.4	59.8
	θ	0.614	0.629	0.871	0.877	0.664	0.598
0.3	IE(%)	68.6	70.4	87.6	88.6	74.5	66.5
	θ	0.686	0.704	0.876	0.886	0.745	0.665
0.4	IE(%)	69.3	71.8	88.4	89.0	82.1	69.2
	θ	0.693	0.718	0.884	0.890	0.821	0.692
0.5	IE(%)	71.7	76.5	90.3	90.9	86.7	74.5
	θ	0.717	0.765	0.903	0.909	0.867	0.745
0.6	IE(%)	78.6	84.5	92.3	93.6	90.1	80.3
	θ	0.786	0.845	0.923	0.936	0.901	0.803
0.7	IE(%)	85.7	91.6	93.1	95.1	91.6	82.3
	θ	0.857	0.916	0.931	0.951	0.916	0.823
0.8	IE(%)	82.9	88.7	91.0	91.4	83.6	79.6
	θ	0.829	0.887	0.910	0.914	0.836	0.796
0.9	IE(%)	81.4	83.1	90.4	90.6	79.2	75.5
	θ	0.814	0.831	0.904	0.906	0.792	0.755

**Figure 1:** Inhibition efficiency of DM extract on mild steel in 1M HCl for different immersion periods, at room temperature, using weight loss method**3.4 Temperature Studies**

The inhibition efficiency increases with increasing temperature. The inhibition efficiency increased up to **333K** temperature and then slightly decreased. This may be due the fact that chemisorption increases with temperature due to the strengthening of chemical bonds, and as a result inhibition efficiency increases with temperatures up to 333K and thereafter the decomposition of the DM corrosion inhibitor may take place. This shows the chemical adsorption takes place on the metal surface. The maximum inhibition efficiency was found to be 98.7% at 333K temperature for 0.7% concentration of the extract.

Table 4: Inhibition efficiency of DM extract on mild steel in 1M HCl for different concentrations using weight loss method at different temperatures.

Conc. (%)		Inhibition efficiency (%)				
		303 K	313 K	323 K	333 K	343 K
0.1	IE (%)	57.1	77.2	88.5	90.8	82.2
	θ	0.5714	0.7720	0.8854	0.9078	0.8224
0.2	IE (%)	61.4	79.7	89.5	91.8	83.5
	θ	0.6143	0.7971	0.8948	0.9180	0.8347
0.3	IE (%)	68.6	83.2	91.7	93.8	85.5
	θ	0.6857	0.8323	0.9168	0.9382	0.8555
0.4	IE (%)	69.3	85.6	94.1	95.2	87.4
	θ	0.6929	0.8558	0.9414	0.9520	0.8739
0.5	IE (%)	71.7	87.1	95.1	96.2	89.2
	θ	0.7171	0.8707	0.9509	0.9625	0.8922
0.6	IE (%)	78.6	90.7	97.0	98.1	91.1
	θ	0.7857	0.9066	0.9697	0.9810	0.9106
0.7	IE (%)	85.7	93.4	97.8	98.7	95.2
	θ	0.857	0.934	0.978	0.987	0.952
0.8	IE (%)	82.9	91.0	96.7	97.7	94.1
	θ	0.829	0.91	0.967	0.977	0.941
0.9	IE (%)	81.4	87.3	93.7	97.4	93.5
	θ	0.814	0.873	0.937	0.974	0.935

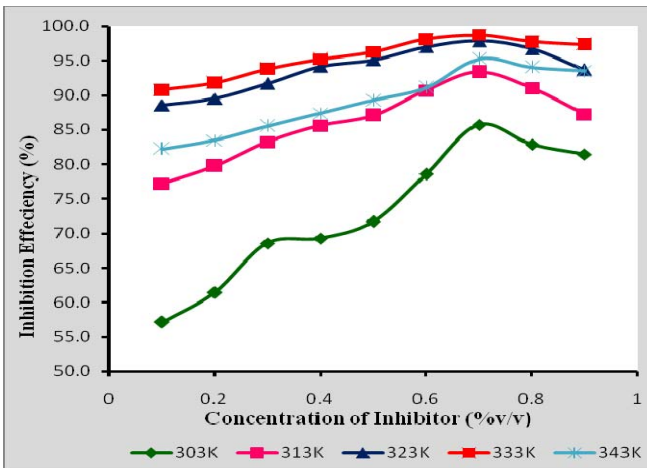


Figure 2: Variation of inhibition efficiency of DM extract, at different concentrations, on mild steel in 1M HCl at different temperature

Energy of activation (E_a) was calculated by Arrhenius equation

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303 \times R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (4)$$

Where,

ρ_1 - the corrosion rates at T_1 temperature, ρ_2 - the corrosion rates at T_2 temperature and 'R' is a gas constant.

The change in free energy of adsorption for different higher temperatures in comparison with room temperature at various concentration of inhibitor was calculated using the equation (3),

$$\Delta G_{ads} = -2.303 \times 8.314 \times T \times \log (K \times 55.5)$$

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$$K = \frac{\theta}{(1 - \theta)C} \quad (5)$$

Where,

θ - Surface coverage of the metal surface, C - Concentration of the inhibitor in percentage

T - Temperature in Kelvin and K - Equilibrium constant.

Table 5: Calculated values of activation energy E_a and free energy of adsorption for mild steel corrosion in 1M HCl with and without acid extract of DM

Conc (%v/v)	E_a KJ/mol	$-\Delta G$ KJ/mol					ΔS KJ/mol	ΔH KJ/mol
		303K	313K	323K	333K	343K		
blank	60.41	-	-	-	-	-	-	-
0.1	36.57	16.62	19.60	22.44	23.80	21.71	0.144	25.67
0.2	37.13	15.32	18.18	20.83	22.24	20.03	0.134	24.24
0.3	37.48	15.09	17.73	20.44	21.96	19.35	0.127	22.26
0.4	34.46	14.45	17.45	20.68	21.90	18.99	0.135	25.00
0.5	31.92	14.19	17.20	20.58	22.00	18.87	0.141	27.18
0.6	30.15	14.66	17.67	21.44	23.43	18.94	0.143	27.00
0.7	25.98	15.51	18.24	21.97	24.13	20.37	0.156	30.39
0.8	29.16	14.63	17.04	20.44	22.15	19.36	0.145	28.37
0.9	28.07	14.08	15.71	18.28	21.37	18.77	0.150	30.92

The positive value of ΔH indicates that the adsorption process is endothermic. ΔG , ΔS and ΔH values do not show any gradual increase or decrease with respect inhibitor concentration. This shows that adsorption of the phytoconstituents is dependent not only on concentration but also on other factors like presence of other constituents, electronic and steric interaction of the inhibitor constituents among themselves as well as with the other constituents present in the corrosive media. Activation energy (E_a) value for blank is 60.41 kJ/mol and 25.97 kJ/mol for 0.7% concentration of the inhibitor. The magnitude of E_a show that the chemical adsorption is involved Sankarapavinasam et al. [10].

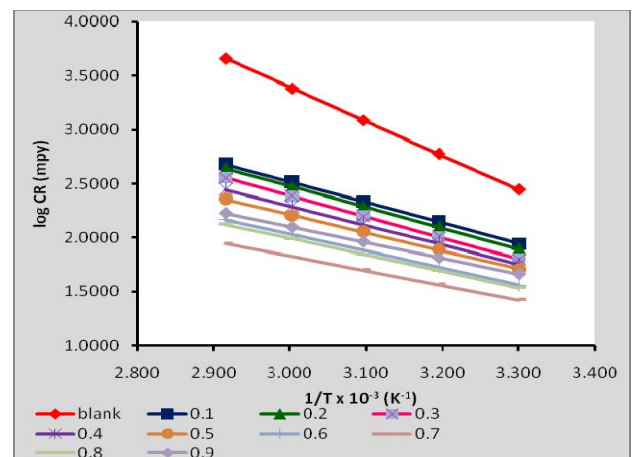


Figure 3: Arrhenius plot for the dissolution of mild steel in 1M HCl with and without DM extract at various temperatures

3.5 Adsorption Consideration

Adsorption isotherm is very important in determining the mechanism of inhibitor. Figure 4,5 shows that the inhibitor follows the Frenmdlich and Temkin adsorption isotherm. This Temkin isotherm is applicable for the chemisorptions of species to form a monolayer on the surface.

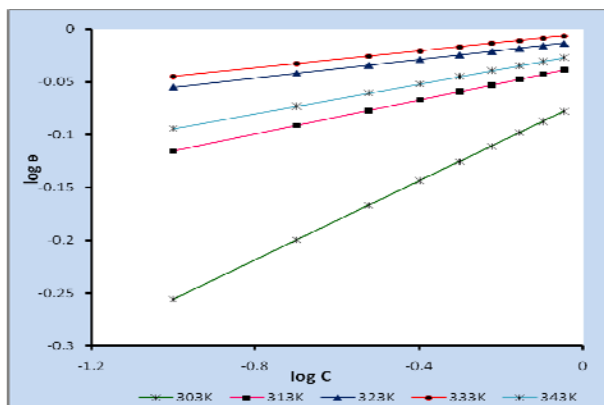


Figure4: Frenndlich adsorption isotherm plot for the different concentrations of DM extract on the mild steel in 1M HCl at 298K and 333K

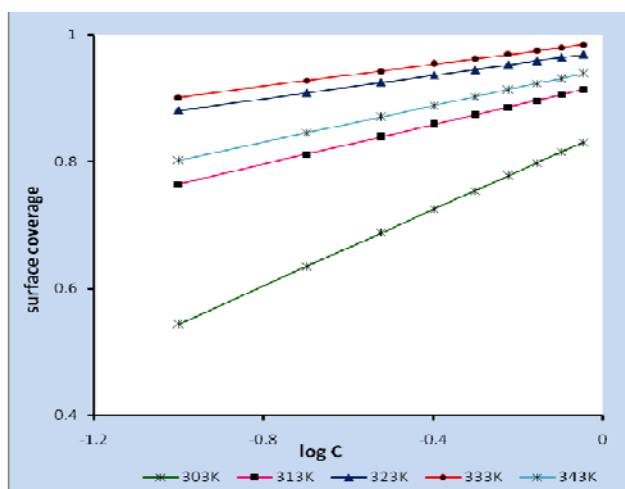


Figure 5: Temkin adsorption isotherm plot for the different concentrations of DM extract on the mild steel in 1M HCl at 303K and 343K

3.6 Tafel Polarization Studies

The concentration of the DM extract increases, the corrosion current decreases. The inhibition efficiency value was also found to increase from 60.85 % to 80.47%. The calculated polarization resistance (R_p) is increased from 67.03 to 324.2 Ωcm^2 with the increase of inhibition efficiency from 56.67 to 79.32% for the concentration of 0.1% to 0.7%. From the results obtained, DM extract is found to be a good corrosion inhibitor. The b_a and b_c values indicates that the mixed type inhibiting both anodic and cathodic reactions.

Table 6: Electrochemical polarization (Tafel) Parameters for the corrosion of mild steel in 1M HCl containing with and without DM extract at room temperature

Con. (%)	$-E_{\text{corr}}$ (mV)	I_{corr}		b_a (mV/dec)	b_c (mV/dec)	R_p	
		(mA/Cm ²)	IE (%)			(Ωcm^2)	IE (%)
blank	502.9	0.412	-	83	125	67.03	-
0.2	475.8	0.161	60.85	65	146	154.7	56.67
0.4	478.6	0.160	61.12	66	144	156.1	57.06
0.7	477.8	0.081	80.47	73	132	324.2	79.32

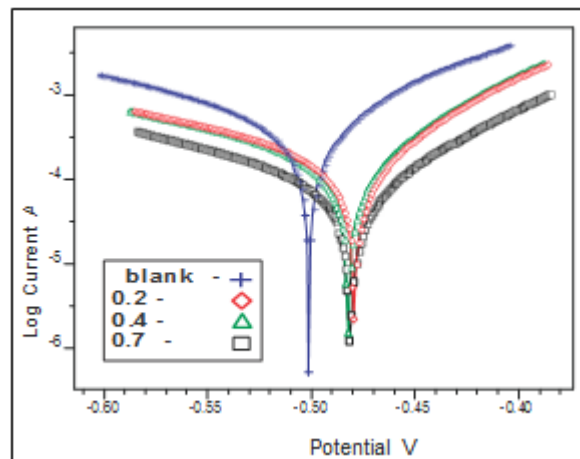


Figure 6: Potentiodynamic polarization curves for mild steel in 1M HCl in the absence and presence of different concentrations of DM extract

3.7 Electrochemical Impedance Measurement

Table 7. shows that the charge transfer resistance (R_{ct}) values has increased from 25.65 to 119.11 Ωcm^2 and the double layer capacitance (C_{dl}) the values had decreased from 53 to 42 $\mu\text{F}/\text{cm}^2$ with increase in concentrations of DM extract. The decrease in C_{dl} values could be attributed to the adsorption of the inhibitor molecules at the metal surface.. The maximum inhibition efficiency obtained for DM extract was 78.46% at 0.7% concentration. The semi circle curves of impedance indicated that the corrosion of mild steel was mainly controlled by charge transfer process.

Table7: Electrochemical impedance parameters for mild steel in 1M HCl containing different concentrations of DM extract at room temperature

Conc.(%)	$R_{ct}(\Omega\text{cm}^2)$	$C_{dl}\mu\text{F}/\text{cm}^2$	IE (%)
blank	25.655	53.14	-
0.2	63.723	49.14	59.74
0.4	75.421	46.42	65.98
0.7	119.111	42.34	78.46

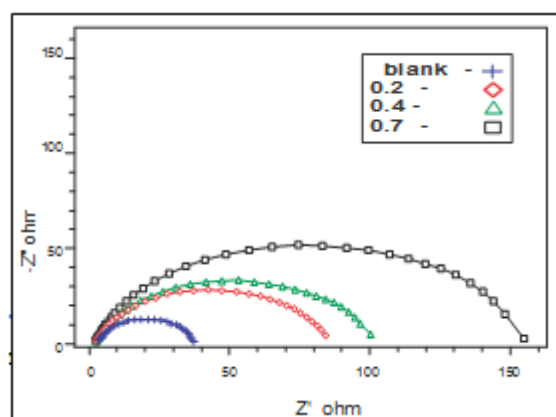


Figure 7: Impedance diagram for mild steel in 1M HCl in the presence and absence of different concentrations of DM extract

4. Conclusion

The extract of DM acts as good and efficient inhibitor for the corrosion of mild steel in 1 M hydrochloric acid medium. The inhibition efficiency increases with concentration, the maximum inhibition efficiency is 98.7 % at 0.7 inhibitor concentration. The inhibition efficiency increases with temperature, it indicates that DM act as a effective inhibitor at high temperature also. The adsorption of inhibitor on surface is spontaneous process. The adsorption of the extract of DM on mild steel obeys Temkin and freundlich adsorption isotherm. A polarization study indicates that indicate the inhibitor to be of a mixed type inhibiting both cathodic as well as anodic reactions.

5. Scope for Future Research

- Surface examination of mild steel specimen may be carried out using Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD) studies.
- The plant extracts studied under investigation may be applied in industries for acid pickling, acid descaling and oil well acidizing purposes.
- Studies may be performed with the plant extracts as well as purely synthesized phytochemical constituents to know the difference in cost of corrosion, the economic importance and also would be helpful in predicting the exact mechanism of inhibition of corrosion.

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